

Water in hybrid perovskites: Bulk MAPbI₃ degradation via super-hydrous state

Cite as: APL Mater. 7, 041112 (2019); doi: 10.1063/1.5087290

Submitted: 31 December 2018 • Accepted: 19 March 2019 •

Published Online: 11 April 2019



Arvin Kakekhani,¹ Radhika N. Katti, and Andrew M. Rappe^{a)}

AFFILIATIONS

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA

Note: This paper is part of the special topic on Perovskite Semiconductors for Next Generation Optoelectronic Applications.

^{a)}E-mail: rappe@sas.upenn.edu

ABSTRACT

Here, first-principles density functional theory calculations are presented which reveal how water incorporation in hybrid halide perovskite [CH₃NH₃]PbI₃ (MAPbI₃) catalyzes the phase transition to the ([CH₃NH₃]PbI₃·H₂O edge-sharing) monohydrate (colorless) phase, eliminating its favorable photovoltaic properties. First, fundamental chemical and electrostatic interactions between water and each component of MAPbI₃ are analyzed, demonstrating their dependence on water concentration. Second, the energetics of incorporated water is explored, leading to the discovery of spontaneous phase segregation into dry regions and regions with more than one water per formula unit—termed the “super-hydrous state.” Third, the properties of the super-hydrous state are analyzed, including the acceleration of octahedron breaking and rearrangement by the high water density. This reveals the phase transformation to be a bulk process, initiated at the super-hydrous regions. This paper concludes with a discussion of how this super-hydrous model explains disparate recent experimental observations concerning the water-induced transition from (black) perovskite to edge-sharing PbI₂ (yellow) phase.

© 2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5087290>

I. INTRODUCTION

Organometal halide perovskites (OMHPs) have been a center of attention in the renewable energy community due to their rapid increase in efficiency as photovoltaic (PV) materials,^{1–10} LEDs, and high-gain photodetectors.^{11–19} Low-cost and low-temperature production methods, high optical adsorption over a broad solar spectrum, sharp band edge, tunable bandgap, and long charge-carrier lifetime and diffusion length have made this class of materials exceptionally attractive.^{20–29} Since 2009, when the top reported power conversion efficiency (PCE) was 3.8%, further development of hybrid perovskite solar cells (PSCs) has enabled efficiencies higher than 23%.^{30–37} Methylammonium lead iodide (MAPbI₃) is one OMHP that has been widely studied.^{38–43} Due to optimal bandgap and long carrier diffusion length, MAPbI₃ is a promising material for PV technology.^{29,44–48} It consists of a perovskite (ABX₃) organic-inorganic hybrid lattice, where the methylammonium (MA) organic A cations sit in the cages formed by the inorganic (BX₃) lead iodide corner-sharing octahedral lattice. The polarity of the methylammonium molecule and its interaction with the

inorganic lattice contribute to the favorable optical and electronic properties of the material which, in turn, make MAPbI₃ a more efficient PV.^{38,49–55}

It has been shown that MAPbI₃ is thermodynamically unstable.^{56–59} Thus, even in the absence of foreign molecules, the material has a tendency to (eventually) degrade.^{60–62} Nevertheless, water molecules can significantly catalyze and accelerate the degradation process.^{38,63–69} Although the presence of moisture has been found to have advantageous effects during the formation and crystallization of MAPbI₃, leading to an improvement of the performance of solar cells,^{70–77} prolonged exposure is known to cause its degradation back to PbI₂. This factor stands as a prominent obstacle to the commercialization of MAPbI₃.^{78–82} Just by placing the material in ambient conditions for 24 h, the PCE of the material drops by up to 80% due to its instability.⁷² Careful device encapsulation schemes have been proposed to avoid the exposure to water and the consequent degradation,^{83–88} although many of these schemes fail to prevent degradation after prolonged aging and exposure to heat and humidity.^{89–92} Experimental studies indicate that the degradation mechanism (from favorable black-phase

perovskite MAPbI₃) first goes through a transformation into a colorless edge-sharing monohydrate (MAPbI₃·H₂O) phase.^{93,94} This transformation is found to be reversible (in the presence of water vapor but not with liquid water), unlike the further transformation to (yellow-phase) PbI₂ (plus CH₃NH₂ and HI).^{93,95–99} Degradation widens the bandgap of MAPbI₃ and eliminates its favorable PV properties.^{100–105}

Most of the theoretical literature has been focused on a surface mechanism in understanding the degradation process.^{106–121} Polarization dependence of water binding energy (BE) on MAPbI₃(001) has been shown.¹²² *Ab initio* molecular dynamics (MD) calculations on different facets of MAPbI₃(001) have also been performed.^{100,123} Force-field based MD has also been applied to study the surface interactions with liquid water and a layer-by-layer degradation.¹²⁴

There have also been some theoretical studies on water in bulk MAPbI₃. For example, Hall *et al.* studied the reversible water intercalation and related this to the water pressure dependence of the cell open-circuit voltage.¹²⁵ They indicated a favorable interaction between H₂O and a hydrogen of the ammonium group (in MA⁺) for low H₂O concentrations. This study involves water BEs up to 0.5 H₂O (per MA) concentration. They observe that the BE per H₂O becomes less exothermic for increasing water concentration (up to the highest coverage they study, i.e., 0.5). Grancini *et al.* made the same observation about the favorability of H₂O–MA⁺ interactions and consider this as the driving force for water incorporation, but they only studied 0.25 H₂O (per MA) concentration.¹⁰¹ Jong *et al.* studied water intercalation in 1 H₂O (per MA) concentration.¹²⁶

II. MOTIVATION

Despite the advances in understanding the instability of perovskite MAPbI₃, there are still important unsolved questions. Specifically, we address four such questions: (i) What is the nature of bonding between water and MAPbI₃, and what are the fundamental forces driving it? To answer this, we perform density functional theory (DFT)-based electronic structure analysis along with appropriately designed numerical experiments. (ii) How does the energetics of water bonding in MAPbI₃ help us to determine the arrangement of water in the solid? To answer this, we compute the concentration dependence of water bonding geometries and energetics, varying the (H₂O:MA) ratio from $\frac{1}{32}$ to 2. (iii) How can the corner-sharing perovskite MAPbI₃ structure readily and in low (room) temperatures turn into an edge-sharing monohydrate phase with a dramatically different structure? To understand this, we analyze the high concentration limit of water intercalation and explain how a super-hydrous state acts as a transient bridge between corner- and edge-sharing structures. (iv) Is MAPbI₃ degradation a bulk or surface-driven mechanism? To answer this, we take few experimental puzzles and explain how a super-hydrous bridge and a bulk degradation mechanism can rationalize them. Some of these experiments include the following: (a) the isotropic and homogeneous reversible formation of the monohydrate phase independent of the depth in the film;⁹³ (b) the scaling behavior of moisture-induced grain degradation in polycrystalline perovskite MAPbI₃;¹²⁷ (c) the observation that grain-boundary passivation enhances the stability of the sample.¹²⁸

III. COMPUTATIONAL METHODS

We perform calculations using density functional theory (DFT)^{129,130} with plane wave basis sets using the Quantum Espresso.¹³¹ Ultrasoft GBRV pseudopotentials¹³² and Perdew, Burke, Ernzerhof (PBE) exchange correlations (XC)¹³³ have been used. Dispersion interactions are accounted for using the Grimme DFT-D2 method.^{134,135} For calculating energy barriers, we use the nudged elastic band method with climbing image (CI-NEB).^{136–139} We use a kinetic energy cutoff for wave functions (E_{cut}) equal to 476 eV and the charge cutoff being 10 times larger. The sampling for k-space is equivalent to $3 \times 3 \times 2$ for the tetragonal MAPbI₃ $\sqrt{2} \times \sqrt{2} \times 2$ supercell containing 48 atoms. The E_{cut} and k-mesh have been chosen to achieve a convergence of better than 0.01 eV for calculating binding energies (BEs). This was checked by increasing E_{cut} up to 1360 eV and increasing the k-space sampling to the equivalent of $9 \times 9 \times 6$ (for more details, see Sec. 1 of the [supplementary material](#)). The BE is defined such that a more negative number means more exothermic

$$\begin{aligned} BE(\text{H}_2\text{O}) &= E_{\text{bind}}(\text{H}_2\text{O}) \\ &= E(\text{Material with H}_2\text{O}) - E(\text{bare material}) \\ &\quad - E(\text{isolated H}_2\text{O molecule}). \end{aligned}$$

For calculating the structures with(out) water, we perform variable-cell relaxations (vc-relax), permitting the atomic coordinates and all components of the lattice vectors to relax. Many (in some concentrations ≈ 100) educated guess-structures (based on the knowledge of H₂O bonding discussed in this work) have been used as initial guesses (starting points) to ensure identification of the global energy minimum.

We successfully achieve a convergence of better than 0.01 eV (for BEs) with respect to our convergence parameters; this is the precision we use in quoting calculated energetics. The theoretical model we propose is self-consistent up to this limit. Furthermore, we have identified the error that might be associated with the absolute values of our BEs (compared to experiments). We have pinpointed the possible errors generated by short and long-range corrections to our XC functional, by benchmarking our results against hybrid functionals and different schemes for inclusion of dispersion interactions. For more details, see Sec. 2 of the [supplementary material](#).

IV. RESULTS AND DISCUSSIONS

A. Fundamentals of water bonding in MAPbI₃

Below, we delve into the nature of water bonding in MAPbI₃. To better understand the system by analyzing different contributions to the bonding, we also perform numerical gedanken experiments on molecular MA⁺ (with negative jellium background) and PbI₃[−] (with positive jellium background).

1. H₂O–MA⁺ bond

In much of the literature, the bond between water and organic MA⁺ group in MAPbI₃ has been named a hydrogen bond.¹⁴⁰ Although here we are not concerned with the semantics, the bonding between MA⁺ and water is fundamentally different from a canonical hydrogen bond, e.g., O–H···O bonds in a water network. The main

TABLE I. Total charges (nuclear + electronic) computed using BCA on MA⁰ and MA⁺ (electron charge is negative). The average charge on N-bound H is denoted as $\bar{H}_N$ and C-bound is denoted as $\bar{H}_C$.

	MA ⁰	MA ⁺	$\Delta(\text{MA}^+ - \text{MA}^0)$
N	−1.27	−1.26	0.01
$\bar{H}_N$	0.31	0.52	0.21
C	0.13	0.28	0.15
$\bar{H}_C$	0.07	0.14	0.07
Sum	0.00	1.00	1.00

difference is that unlike a neutral H₂O molecule, the MA⁺ group has a net +e charge, and the presence of this extra hole has a determinative role in dictating the strength of the H₂O–MA⁺ bond. To elucidate this, we investigate H₂O bonding to MA⁺ and MA⁰ molecules. Both molecules are placed in large boxes and isolated using the Martyna-Tuckerman scheme.¹⁴¹ It turns out that the H₂O BE to cationic MA⁺ is −0.86 eV, while the BE to MA⁰ is only −0.45 eV. Thus, the hole on the MA⁺ makes a great contribution to the bond. To better understand the spatial distribution of this hole and how this changes upon water bonding, we use the Bader charge analysis (BCA).^{142,143} As can be seen in Table I, the hole on MA⁺ is mostly located on N-bound hydrogens ($\bar{H}_N$). Thus, these hydrogens are more “proton-like.” This is the reason H₂O binds to one of these hydrogens. In Table II, after H₂O binds to an $\bar{H}_N$ (we denote this specific hydrogen by $\bar{H}_N^*$), (a) the $\bar{H}_N^*$ becomes even more proton-like, i.e., the hole redistributes itself to move more toward an H₂O lone-pair, and (b) the associated N–H bond is elongated. This shows itself as the blue region (electron depopulation) localized on this hydrogen in Fig. 1(c). The aforementioned N–H bond elongation phenomenon is also observed in the context of surface chemistry and is known as adsorbate-induced lifting.^{144–146} The common cause is creating a deeper electrostatic potential well (and a stronger associated electric field) that can more strongly polarize and bind the H₂O lone-pair.¹⁴⁴ In Table II, in addition to localization of the hole on $\bar{H}_N^*$, MA⁺ electrons also get more localized on the CH₃ group to decrease the electron-electron repulsion with the polarized lone-pair. There is also a small charge transfer from

H₂O to MA⁺ which stems from some degree of covalency and orbital mixing.

The role of local electric fields and electrostatic potential wells (ESP wells) in enhancing water bonding via lone-pair polarization has been recently pointed out in the context of inorganic surface chemistry;¹⁴⁴ we extend such a picture to the bulk chemistry of hybrid organic-inorganic systems. The chemically active lone-pair orbitals of water are its HOMO (perpendicular to its dipole) and HOMO-1 (parallel to its dipole), which are shown in Figs. 1(a) and 1(b). Figures 1(c) and 1(d) show the water lone-pair (specifically HOMO-1) polarization upon interacting with MA⁺. The lone-pair polarization puts more electron charge density closer to the proton-like $\bar{H}_N^*$, close to which a deep electrostatic potential well (and associated strong electric field) exists [this charge movement is indicated by the yellow arrow along O–MA bond in Fig. 1(c)]. Figures 1(c) and 1(d) reveal that the charge density differences are virtually identical using B3LYP and PBE-D2 XC functionals. It can also be seen that there is some electron charge movement toward the CH₃ group (as also mentioned above in the context of changes in Bader charges) to minimize the electron-electron repulsion between the polarized lone-pair and the MA. The latter charge redistribution is indicated by a yellow arrow along the N–C bond in Fig. 1(c).

In addition to the electrostatics, there is also a (less dominant) covalent component to the H₂O–MA⁺ bond. This is noticeable in the BCA presented above, showing itself as a small charge transfer from H₂O to MA⁺. This covalency also shows up as a bifurcation of water HOMO-1. For more details, see Sec. 3 of the [supplementary material](#).

2. H₂O–PbI₃[−] bond

Here, to identify and better understand the different binding motifs in the full MAPbI₃ system, we design another gedanken experiment: take the fully vc-relaxed MAPbI₃ supercell, remove the MA⁺ cations, and substitute them with a uniform positive jellium. We then relax the remaining PbI₃[−] cell, fixing the lattice parameters. The goal is to understand how the inorganic backbone can bind H₂O, independent of specific organic groups.

Figure 2 depicts the structure of the bare PbI₃[−], the H₂O binding geometry to the Pb²⁺ cation, and the associated charge density difference plots. In our PbI₃[−] model, as well as MAPbI₃, the Pb²⁺ cations are encaged at the center of I₆ octahedra. Such a symmetric

TABLE II. Total charges (nuclear + electronic) computed using BCA and bond lengths for bare MA⁺ before binding to H₂O and MA⁺ after H₂O bonding.

MA ⁺	N–H bond length (before) Å	Charge (before)	N–H bond length (after) Å	Charge (after)
$\bar{H}_N^*$	1.036	0.52	1.075	0.58
$\bar{H}_N$			1.034	0.50
	Charge (before)		Charge (after)	
H ₂ O	0		0.07	
N	−1.26		−1.21	
NH ₃	0.3		0.38	
CH ₃	0.7		0.56	

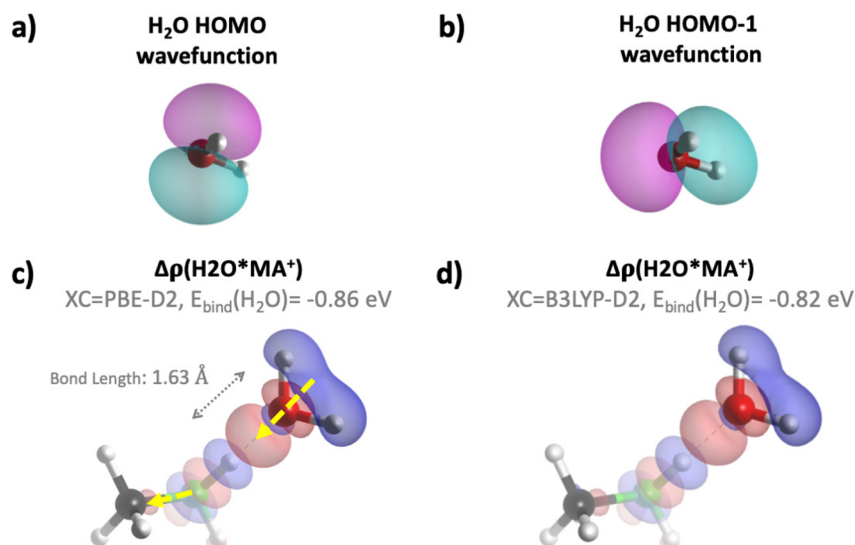


FIG. 1. (a) and (b) depict the H₂O chemically active orbitals (HOMO and HOMO-1). Cyan and magenta show different signs of the wavefunction. (c) and (d) show the electron charge density difference upon water bonding to MA⁺ derived using (c) PBE-D2 and (d) B3LYP-D2 XC functionals. Red (blue) shows the regions populated (depopulated) by electrons. The yellow arrows in (c) show the direction of local charge density movement. Color code is O(red), H(white), C(black), and N(green).

distribution of negative charges around the positive centers causes a relatively insignificant electrostatic potential well outside the Pb²⁺ center. Alternatively, one can think of this as an effective screening of the Pb²⁺ electric field by the I₆ symmetric cage, preventing bond formation between the H₂O lone-pair and the Pb²⁺. Only when such an octahedron is broken [see Fig. 2(b)], Pb²⁺ moves off-center and

some ∠I – Pb – I angles are widened [see the ∠I₃ – Pb – I₄ in Fig. 2(c)], and there is an appropriate angle of approach in which the Pb²⁺ positive center is far enough from the surrounding I[−] such that a significant electrostatic potential well (and associated electric field) can be accessed close to Pb²⁺ by the H₂O lone-pair. Here, the Pb²⁺ is no longer at the center of the asymmetrical I₆ cage. This is shown

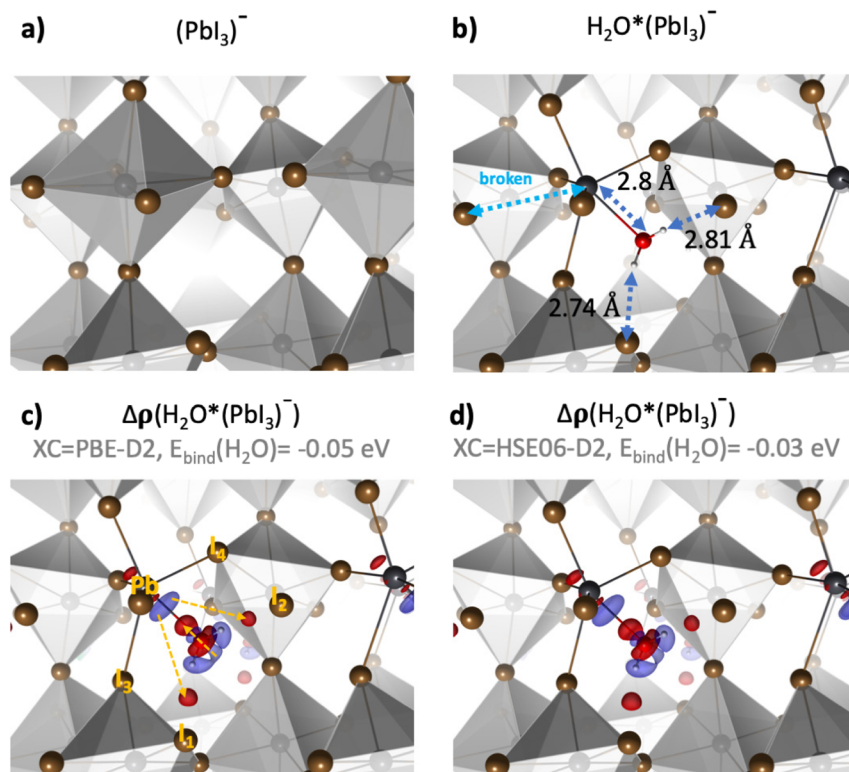


FIG. 2. (a) The PbI₃[−] structure, (b) H₂O binding to PbI₃[−], and the associated charge density difference plots for (c) PBE-D2 and (d) HSE06-D2 XC functionals. The water concentration is 0.25 H₂O:Pb. Red (blue) shows the regions populated (depopulated) by electrons. The orange arrows in (c) show the direction of local charge density movement. Color code is O (red), H (white), I (brown), and Pb (dark gray).

in Fig. 2(b). This water-induced distortion (symmetry-breaking) has the same principles as the adsorbate-induced lifting in water–surface bonds.¹⁴⁴ Also similar to the case of surfaces, the H₂O bonding geometry is such that the HOMO (perpendicular to H₂O classical dipole) points toward Pb²⁺. The HOMO thus becomes polarized, creating a dipole perpendicular to the water geometric dipole. This is shown in Fig. 2(c) by the orange arrow pointing toward Pb²⁺.

H₂O bonding to the inorganic framework is a triaxial phenomenon [see Fig. 2(c)], associated with three charge accumulation centers: one between O and Pb²⁺ and two between H₂O and I[−]s [marked by I₁ and I₂ in Fig. 2(c)]. A water lone-pair (mostly HOMO) polarizes toward the positive center on Pb, while some charge density on Pb gets re-distributed (to minimize electron–electron repulsion with the polarized lone-pair and create a more positive site toward which the lone-pair polarizes) and localized in the two I[−]–H⁺ axes [between H₂O hydrogens and I₁ and I₂ in Fig. 2(c)]. This can be considered as a hydrogen bond between the H₂O hydrogens and the lattice I[−] ions. Also for a similar reason, some charge density on Pb redistributes to the opposite side of the atom [this can be noticed as the red center at the top-left of the marked Pb in Fig. 2(c)]. Both the shape of charge density re-distribution and the projected density

of states (PDOS) [see Fig. 3(a)] teach us that this triaxial bonding is driven by electrostatics rather than covalency. In Fig. 3(a), the four H₂O peaks below the Fermi energy (E_F) correspond to eight states occupied by electrons in molecular H₂O. In Fig. 3(a), the H₂O chemically active orbitals (HOMO and HOMO-1) remain virtually molecular-like (associated with small broadening and sharp peaks) upon the triaxial interaction with the inorganic backbone. This is the fingerprint of a non-covalent bond. For more information on triaxial bonding and short continuum of states above 5 eV, see Sec. 4 of the [supplementary material](#).

3. H₂O–MAPbI₃ bonds

Based on this understanding of H₂O–MA⁺ and H₂O–PbI₃[−] bonds, we now analyze water bonding to MAPbI₃. So far, there are two distinct water binding sites available for H₂O: (a) interacting with an H_N on MA⁺ and (b) distorting an octahedron and interacting with the exposed Pb²⁺. Based on H₂O BEs reported above, the bonding to MA⁺ seems more favorable. This is also confirmed by our direct MAPbI₃ calculations and the literature.^{125,126} Although studying the H₂O bonding to MA⁺ and PbI₃[−] separately teaches us important lessons on water–MAPbI₃ bonds, there are significant complexities that arise only when considering the whole MAPbI₃

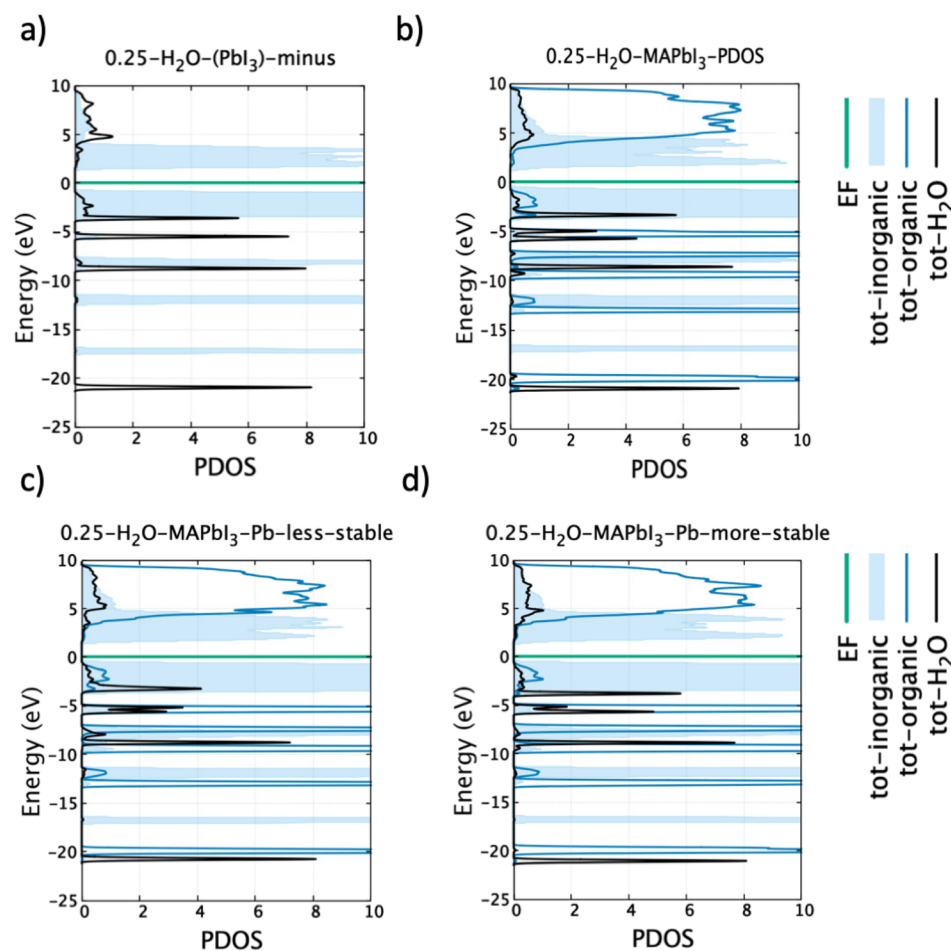


FIG. 3. PDOS of inorganic, organic, and water components for (a) H₂O binding to Pb in PbI₃ (in 0.25 H₂O:Pb concentration), (b) H₂O bonding to H_N⁺ (MA) in MAPbI₃ and H₂O bonding to Pb in MAPbI₃ [in 0.25 H₂O:Pb (MA) concentration] for (c) the less stable local minimum and (d) the more stable H₂O–Pb bond motif.

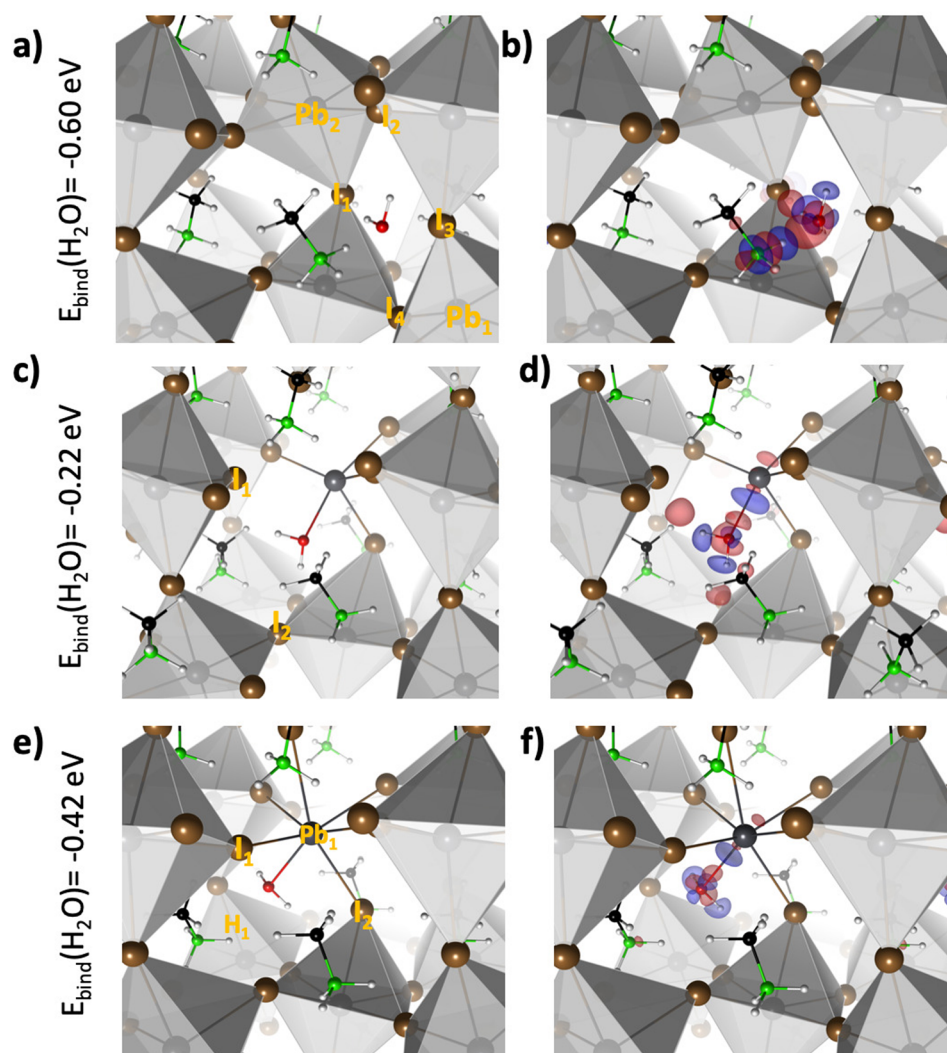


FIG. 4. Different modes of H_2O binding (in 0.25 $\text{H}_2\text{O}:\text{MA}$ concentration) to MAPbI_3 (left) and associated charge density redistribution plots (upon H_2O bonding) (right). Red (blue) shows the regions populated (depopulated) by electrons. In (a) and (b), the lowest-energy binding mode for water is depicted (MA^+ bonding). In (c) and (d), a higher-energy Pb^{2+} bonding mode is depicted which is similar to the previously discussed mode in PbI_3^- (with positive jellium). In (e) and (f), a lower energy Pb^{2+} bonding mode is depicted. Color code is O (red), H (white), C (black), N (green), I (brown), and Pb (dark gray).

system. We examine these, first for the case of relatively low 0.25 $\text{H}_2\text{O}:\text{MA}$ concentration.

First, we consider the more energetically favorable case of H_2O binding to H_N on MA^+ [Figs. 4(a) and 4(b)]. One difference with the simpler case of bonding to a molecular MA^+ is that here water is oriented such that mostly the HOMO lone-pair interacts with the H_N^+ . The HOMO is polarized, putting more charge density closer to the electrostatic potential well near the positively charged H_N^+ . Another difference is the existence of H-bonds between H_2O and nearby I^- anions. This can be seen in Figs. 4(a) and 4(b) as the red region between H (of H_2O) and I_1 , which are 2.52 Å apart. Smaller isovalues in the charge density difference plots reveal another red region between the other H and (I_2) 2.73 Å apart: a weaker H-bond. Hence, this can also be considered as a triaxial water bonding environment. It should be noted that although the water does not appear to disrupt the perovskite MAPbI_3 inorganic network, one can quantify some

distortions to the lattice structure (for more details, see Sec. 5 of the [supplementary material](#)).

We now consider the Pb-bonding mode for H_2O . There are two such modes as local energy minima [see Figs. 4(c) and 4(e)]. The less stable bonding mode [Fig. 4(c)] is similar to the H_2O bonding mode to PbI_3^- . In Fig. 4(d), one can notice a triaxial bonding between the H_2O and the inorganic backbone. Water has disrupted the octahedron and exposed the Pb^{2+} , stabilizing its polarized lone-pair in the local electrostatic potential well. It also forms H-bonds with I_1 and I_2 sitting 2.45 and 2.52 Å apart from its hydrogens, respectively.

The second (more favorable) Pb^{2+} bonding mode [Figs. 4(e) and 4(f)] is not favored in the simple case of water in PbI_3^- . Here, the octahedron is not as distorted as the other Pb-bonding mode (or Pb bonding mode in PbI_3^-); thus, less mechanical deformation cost is imposed upon the system. For more details, see Sec. 6 of the [supplementary material](#).

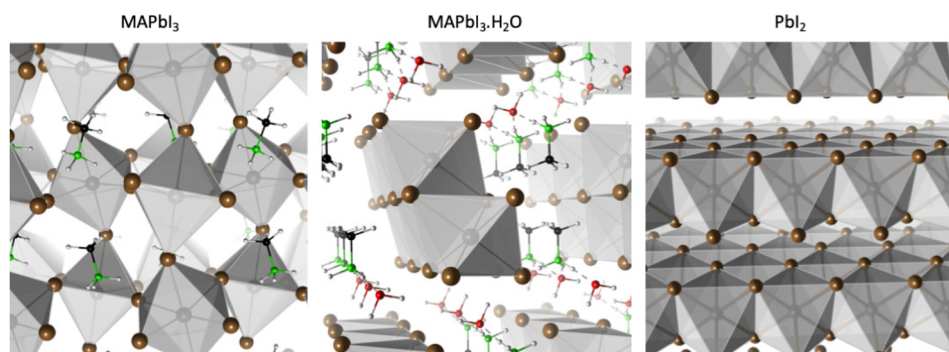


FIG. 5. The structures of corner-sharing MAPbI₃ perovskite (left), edge-sharing monohydrate (middle), and edge-sharing stacked two-dimensional hexagonal PbI₂ (right). Color code is O (red), H (white), C (black), N (green), I (brown), and Pb (dark gray).

4. Water bonding in edge-sharing MAPbI₃·H₂O monohydrate

The reversible degradation of corner-sharing perovskite MAPbI₃ (black phase) to the edge-sharing MAPbI₃·H₂O monohydrate (colorless phase) is a precursor to the irreversible degradation to edge-sharing stacked hexagonal PbI₂ (yellow phase) (see Fig. 5).^{93,147,148} The mechanism behind water binding in the colorless phase is not different from the cases discussed above. This is explained in Sec. 7 of the [supplementary material](#).

B. Concentration-dependent water energetics in bulk MAPbI₃ and phase-segregation

In Fig. 6, we plot the H₂O BE (per molecule), which is the energy gain by addition of water to the material's structure, as a function of H₂O concentration in perovskite MAPbI₃. The general trend is as follows: in a very low concentration, the energy gain by

H₂O intercalation (H₂O BE) into perovskite MAPbI₃ is ~ -0.68 eV per molecule. This limit is a local minimum in the space of BE vs H₂O concentration (n , defined as H₂O:MA ratio). As we increase H₂O concentration, the BE per molecule decreases in magnitude (less exothermic) and we reach a maximum at around $n = 1$. Increasing n further leads to stabilization of H₂O intercalation and we reach an almost flat valley at around $n = 2$, which we call a super-hydrous state [see Fig. 7(d)]. In Fig. 6, we also depict the energy gain of turning the water-intercalated perovskite structure into a monohydrate edge-sharing phase (-0.28 eV per H₂O) at $n = 1$. The energy values in Fig. 6 should be compared to the energy associated with the standard entropy of gas phase water (1 bar, 300 K) ~ -0.59 eV. The BEs are great enough that the water intercalation in MAPbI₃ becomes relevant, although such adsorption deprives the molecule of its gas phase translational entropy.

Ranging from $n = 0$ to 1, each H₂O binds to the H_N group on MA⁺, and thus, it might not be obvious why there is a strong

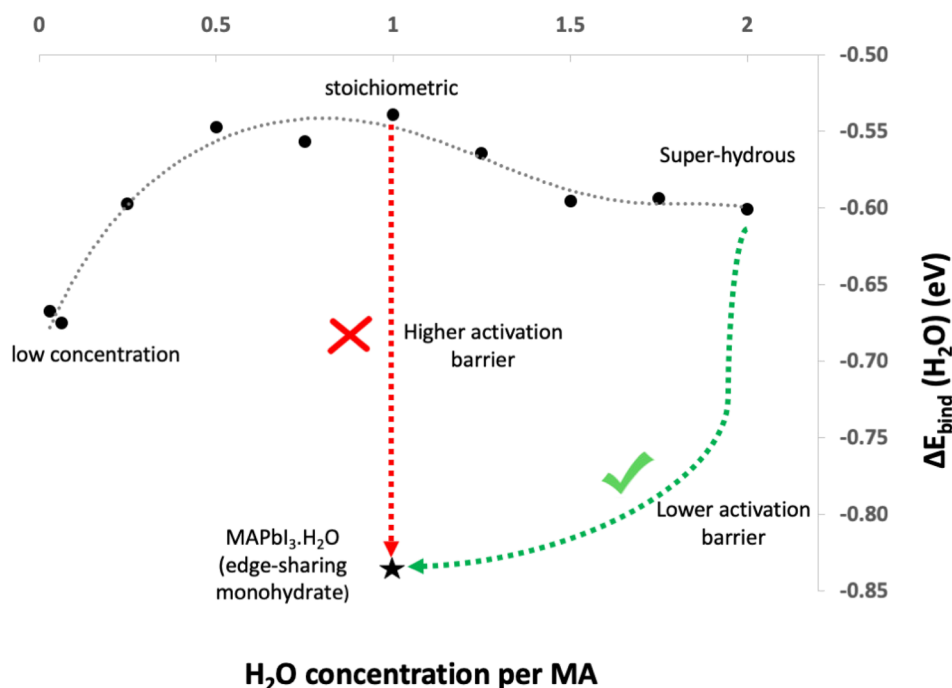


FIG. 6. The H₂O BE (per molecule) as a function of H₂O concentration (H₂O:MA) in MAPbI₃ perovskite are shown by black filled circles. Each H₂O at $n = 1$ gains -0.28 eV stability if the structure changes to the edge-sharing phase: this is shown by the black star. The minimum-energy path to the edge-sharing monohydrate passes through the super-hydrous state.

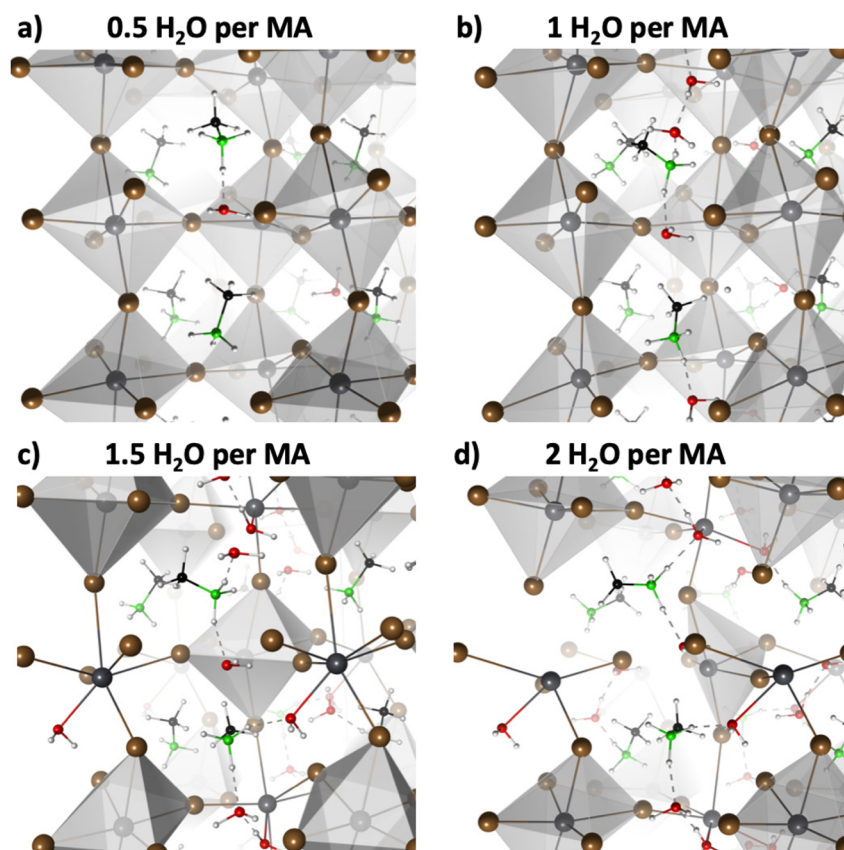


FIG. 7. Ground state water structure for different $\text{H}_2\text{O}:\text{MA}$ concentrations. At over-stoichiometric $\text{H}_2\text{O}:\text{MA}$ ratios, PbI_6 octahedra begin to break by H_2O molecules binding to them. This makes the structure ready for its transformation to the edge-sharing monohydrate form ($\text{MAPbI}_3 \cdot \text{H}_2\text{O}$). Color code is O (red), H (white), C (black), N (green), I (brown), and Pb (dark gray).

n -dependence on H_2O BE. The answer to this is multi-fold. First, each H_2O perturbs (distorts) the inorganic backbone, to maximize the attractive H-bonding to I^- and to minimize the electrostatic repulsion between the O_{2p} lone-pair and I^- . Thus, intercalated water in these materials (even if it is directly interacting with MA^+ in lower concentrations) is surrounded by a network of distortions in the inorganic framework. Thus, increasing the H_2O concentration (from $n = 0$ to 1) leads to unfavorable interactions between these distortions and destabilizes the H_2O binding. Second, the hole-localization on MA^+ is also n -dependent. As mentioned previously, the hole on MA^+ becomes concentrated on the H_N interacting with H_2O , to make it more proton-like. In the case of two water molecules interacting with the same MA^+ , an extra effect changing the BE will be their competition for this hole. In addition to the previous two effects which destabilize H_2O binding, a third (stabilizing) effect in higher concentrations is the possibility of forming H-bonding networks between neighboring H_2O molecules. The existence of these sometimes opposing effects makes it hard to *a priori* make a unique guess for the H_2O binding geometry in MAPbI_3 . In Fig. 7(b), our calculations reveal at $n = 1$, which is four H_2O per our simulation unit cell, the ground-state configuration is the one in which two of the H_2O molecules form a H-bond with each other and through that make a connected chain of $(\text{H}_2\text{O}-\text{MA}-\text{H}_2\text{O}-\text{H}_2\text{O}-\text{MA})$, leaving the fourth H_2O out of the chain to bind to two neighboring MA^+ .

In Fig. 6, at ($n > 1$) range, there is a wide “valley of stability,” which we call a super-hydrous state. In this plot, we have only investigated concentrations as high as $n = 2$, but it is possible that a super-hydrous state continues to be (more) stable even with a larger number of H_2O molecules per unit-cell. As can be seen in Fig. 6, water prefers to phase-segregate into regions of high and low concentrations. Thus, the way to the stable edge-sharing $\text{MAPbI}_3 \cdot \text{H}_2\text{O}$ monohydrate (colorless) phase (which as shown in Fig. 6 is a local thermodynamic sink for the hydrated system) is not a straight way that simply connects a stoichiometric water intercalated $\text{H}_2\text{O}-\text{MAPbI}_3$ (perovskite) phase to the colorless phase, but rather a “longer” path which passes through the phase-segregated valley of stability, i.e., the super-hydrous $n\text{H}_2\text{O}-\text{MAPbI}_3$ ($n > 1$) phase (see Fig. 6). It is only in this super-hydrous state that the structure has enough freedom (associated with lower transformation barriers) to readily re-arrange into an edge-sharing structure. This is due to the broken octahedra and under-coordinated (water-coordinated) Pb^{2+} and I^- ions (see Fig. 7), in addition to emergence of water H-bond networks. Relevant features that can be seen in, e.g., Fig. 7(d), are (a) I^- anions connected to only one Pb^{2+} , (b) Pb^{2+} cations bonding to two H_2O , and (c) connected $\text{Pb}-\text{H}_2\text{O}-\text{H}_2\text{O}-\text{MA}-\text{H}_2\text{O}-\text{Pb}$ strings. In other words, the catalytic role of water for readily driving the phase-transition (around room temperature) through smaller barriers emerges in such an over-hydrous phase.

C. Bulk degradation mechanism via the super-hydrous state

1. High water concentration: Facile octahedra breaking and structural changes

As we have seen previously, the Pb binding mode for H₂O is a higher energy but still competitive mode for lower H₂O concentrations (Fig. 4). For $n = 0.25$, the MA⁺ and Pb²⁺ water binding modes are -0.60 and -0.42 eV, respectively. Although the Pb bonding modes are higher energy at low coverage, as the water molecules keep distorting and expanding the MAPbI₃ cell, upon intercalation, there reaches a point (at $n > 1$) at which the Pb bonding modes are energetically favorable for the system. This causes the structures with broken octahedra to actually become the ground state of the system in the presence of enough water. The exposed Pb²⁺ cations can generate strong electrostatic potential wells that can effectively polarize the H₂O lone-pair and make strong bonds to it.¹⁴⁴ To do this, it is necessary that the symmetry of the PbI₆ octahedron is broken, creating angles of approach along which the water can see a large effective positive charge. As mentioned previously, this is associated with a mechanical deformation energy; thus, Pb bonding modes are not the ground state for water binding at low coverages. By contrast, at higher H₂O concentrations, the structure is automatically pushed in the direction of distortion and disconnectivity. Now, there are enough water molecules that, through forming strong bonds (lone-pair, hydrogen or triaxial bonds) to the MAPbI₃ ionic components and via hydrogen bonding networks with other H₂O molecules, stabilize such distortions (e.g., under-coordinated Pb²⁺ sites).

As can be seen in Fig. 8, at near-zero H₂O concentration regime, the cell volume remains almost constant, or even decreases slightly by water intercalation, mostly due to dispersion interactions.¹⁴⁹ As the water molecules (and their associated distortions in the inorganic-backbone) get closer (by increasing n), the lattice expands to accommodate these distortions and added volume of water molecules. Up to $n = 1$, the added cell volume by water addition is small. Changing n from 0.5 to 1 by the addition of two H₂O

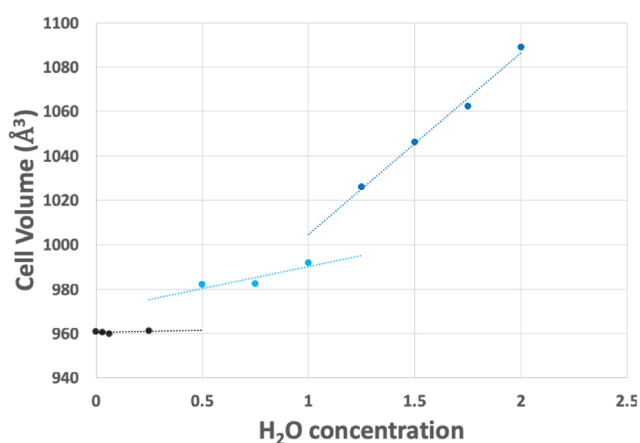


FIG. 8. MAPbI₃ cell volume change upon water intercalation in three different regimes of (H₂O:MA) concentration.

molecules per supercell changes the cell volume by $\approx 5 \text{ Å}^3$ per H₂O, which is small compared to the effective volume of an H₂O molecule in liquid water is $\approx 30 \text{ Å}^3$. At $n > 1$ regime, something special happens. Here, the added cell-volume by addition of each extra H₂O jumps up to $\approx 20 \text{ Å}^3$. The corner-sharing perovskite MAPbI₃ structure can be considered to be broken for $n > 1$. Here, water begins to interact with the Pb²⁺ cations by breaking the PbI₆ octahedra. The large volume expansion per additional H₂O, along with the broken octahedra and associated distortions, gives the super-hydrous structure more freedom to re-arrange into the monohydrate edge-sharing phase. This is another indicator [in addition to the thermodynamic phase-segregation argument (Fig. 6)] that a low (room) temperature transition to the monohydrate phase is facilitated through a super-hydrous pathway. The fact that at $n > 1$, the structure is broken and addition of each water molecule introduces even more distortion and under-coordinated sites, indicates that the super-hydrous state might not be a stable phase (deep enough Gibbs free energy local minimum). Such a phase rather acts as a transient intermediate state between the perovskite and edge sharing structure.

The fact that something special happens at around ($n > 1$) is not only evident in volume-vs-concentration plot (Fig. 8) but also in bandgap-vs-concentration plot [see Fig. 9(a)]. The blue curve depicts the changes in the bandgap of the water intercalated system. The orange curve corresponds to a gedanken experiment done to understand the role of water in changing the materials' bandgap: we remove the H₂O molecules from the relaxed structure, freeze the rest of the structure, and find the electronic structure to calculate the bandgap. It can be seen that in the ($0 \leq n \leq 1$) range, addition of water generally increases the bandgap,¹⁵⁰ and both the hydrated (blue) and H₂O-removed (orange) curves virtually overlap with each other. This gap change is due to the structural deformation and lattice expansion.^{151,152} Generally speaking, the addition of water reduces the connectivity of the MAPbI₃ host structure, weakening bonds, narrowing the bands, and increasing the bandgap.^{152,153} It can be seen in Fig. 9(a) that in the ($1 < n \leq 2$) range, the orange and blue curves begin to deviate from each other. Here, the effect of water cannot be reduced to merely changing the geometric properties of the host MAPbI₃ structure, rather as in Figs. 9(b) and 9(c), the water molecules have a "chemical" role in dictating the bandgap. It can be noted by comparing Figs. 9(b) and 9(c) that at higher water concentrations (e.g., $n = 2$), the water orbitals (more significantly) constitute both the valence band minimum (VBM) and conduction band maximum (CBM), due to an increased covalency with I[−] and Pb²⁺ of the inorganic backbone. This is caused as a result of broken octahedra and water directly making bonds to the inorganic backbone (i.e., the Pb²⁺).

2. Water shuttling to wet regions through bulk MAPbI₃

The energetics of water binding vs concentration in Fig. 6 shows that water intercalation and segregation into high and low concentration regions is energetically favored for the hydrated MAPbI₃ system. But how favorable is the associated dynamics? We calculate the water diffusion barrier (in low concentration $n \approx 0.0625$ or $\frac{1}{16}$) along different possible pathways across the perovskite material. The corresponding minimum-energy paths (MEPs) for water

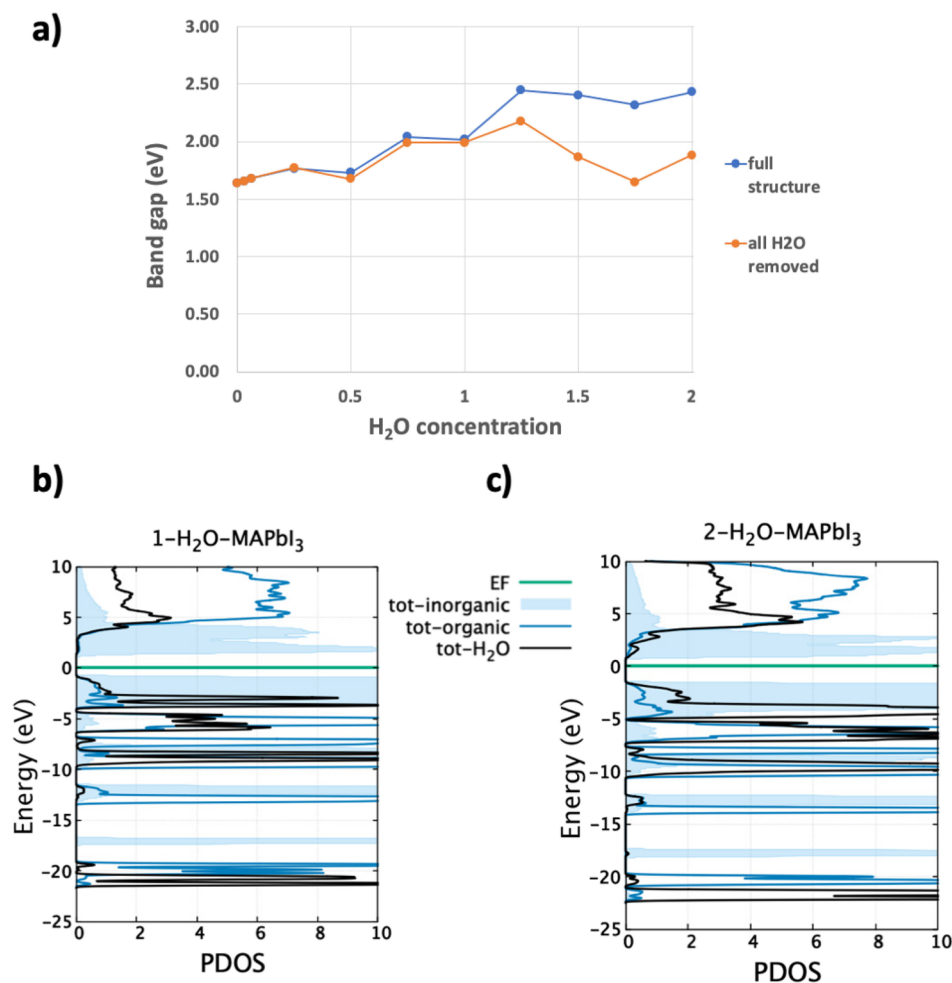


FIG. 9. The change in the MAPbI₃ bandgap upon water intercalation as a function of water concentration (H₂O:MA) is shown in (a). The blue dots are the calculations done on the whole cell (H₂O + MA), while the orange dots are gedanken experiments done by removing the water from the structure, freezing the rest, and solving for the electronic structure. In (b) and (c), the PDOS for two water concentrations (i.e., 1 and 2 H₂O:MA) is shown.

diffusion in the *ab* plane (*a* and *b* represent short axes of the tetragonal phase) and along the *c* axis (the longer direction) are found and depicted in Figs. 10 and 11. The diffusion barrier for the latter is found to be 0.39 eV, while for the former, it is 0.44 eV. These small values, along with the small barriers reported in the literature for water entrance from the vacuum into the material,^{116,122} mean that MAPbI₃ is isotropically permeable to water molecules. Such fast diffusion of water in low concentrations is also supported by experimental observations and has been described by Müller *et al.* as fast and inconspicuous.¹⁵⁴

An important point to note in the MEPs along both long- and short-axis diffusion pathways is the critical role of the electrostatic bond between the proton-like H_N group of MA⁺ and the water lone-pair (HOMO). It can be seen in Fig. 10 that the first MA⁺ rotates such that its H_N group always points at the H₂O HOMO. After reaching the TS2, the water HOMO is locked to the H_N group of the second MA⁺ and both rotate to bring the H₂O into its final state. The same effect can be seen for the long-axis diffusion (see Fig. 11). Here, the H_N group of the first MA⁺ group is locked into the H₂O HOMO, and both MA⁺ and H₂O rotate until water reaches its local energy

minimum at the bottom of its initial cell (image #10 of Fig. 11). Then, the second MA⁺ (at the bottom cell) begins to rotate and bring its H_N group closer to the H₂O. The H_N group then (electrostatically) locks into the water HOMO, and the MA⁺ and H₂O rotate with each other to lead H₂O to its final state.

D. Connection to experiments

Our proposed degradation mechanism via bulk water shuttling and a phase-segregated super-hydrous state can be readily applied to understand some important experimental observations in the literature. Leguy *et al.*⁹³ reported that the formation of the monohydrate edge-sharing MAPbI₃ (colorless) phase is independent of the depth in the film, which is isotropic and homogeneous. Wang *et al.* reported the scaling behavior of moisture-induced grain degradation in polycrystalline MAPbI₃ and mention that grains degrade along the in-plane direction (from grain boundaries toward their center) rather than the out-of-plane direction (from surface down), and that the necessary duration for films to degrade showed a linear relationship with the grain size.¹²⁷ Niu *et al.* demonstrated

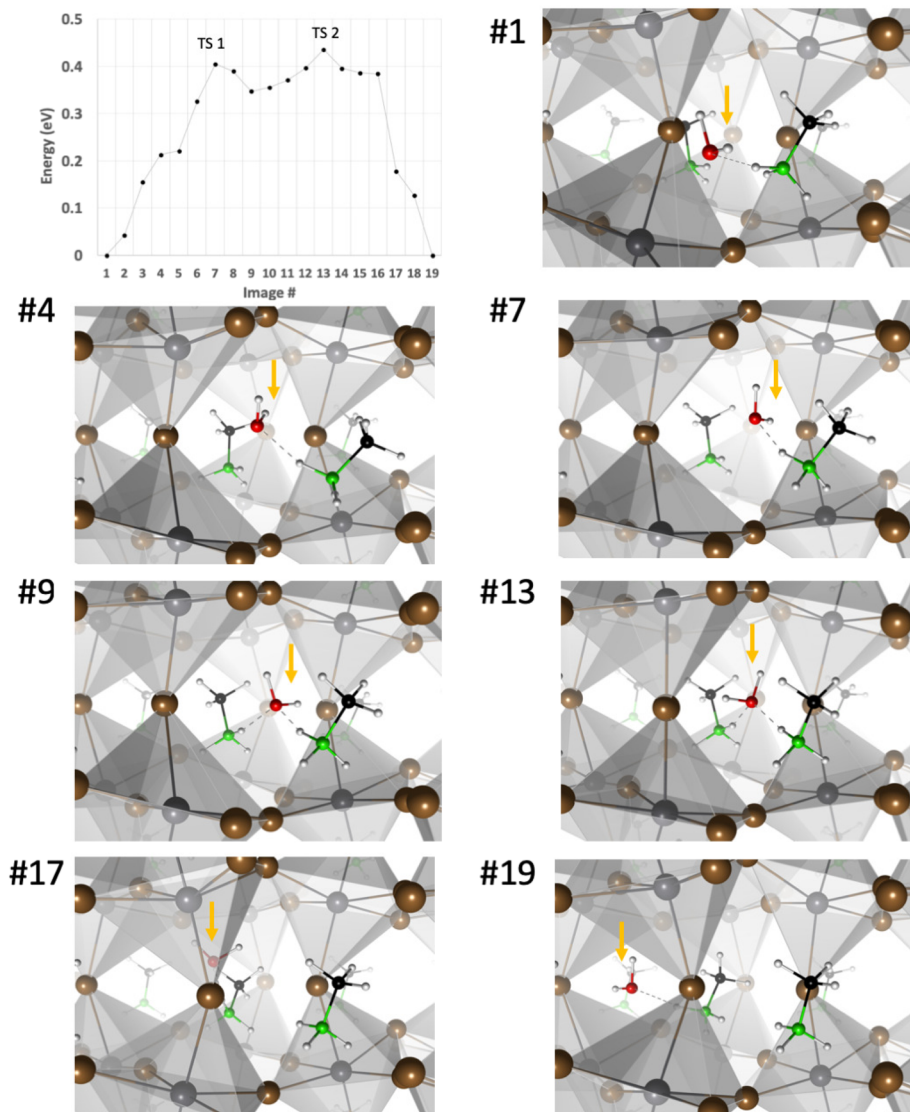


FIG. 10. Minimum-energy pathway for H₂O diffusion at low concentrations in *ab* plane. A few important images are shown, including the first TS image #7 and second TS image #13. As a guide to the eye, the diffusing H₂O is shown by the orange arrow. Color code is O (red), H (white), C (black), N (green), I (brown), and Pb (dark gray).

an effective mechanism to enhance the stability of the sample via grain-boundary passivation with hydrophobic agents.¹²⁸ As shown in Fig. 6, although the presence of a low concentration ($n \lesssim 0.1$) of water molecules is energetically favorable for the system, but as the energy vs concentration has a positive slope for $0 \leq n \leq 1$, each H₂O makes the local environment more hydrophobic. On the contrary, if there is a nucleus of a larger concentration of H₂O molecules ($n \approx 2$), the addition of extra water molecules does not affect the energetics of the rest due to the zero slope of energy vs concentration in this limit. Consequently, such a nucleus grows, which can then transform the local environment toward the lower-energy colorless phase (see Fig. 6). We propose that these initial high concentration nuclei are located in grain boundaries due to a large concentration of structural and stoichiometric defects and the related free volume.¹⁵⁵ Next, since the H₂O molecules can easily shuttle through

the material,¹⁵⁴ they find these high-concentration nuclei (“wet” regions) get adsorbed into them, leaving the “center” of the grains as low concentration (“dry”) regions behind. This is the reason why the degradation propagates “in-plane” from the grain boundaries toward the center.^{127,156} We propose that the homogeneity reported by Leguy *et al.*⁹³ and the thickness independent degradation rate mentioned by Wang *et al.* are the result of two operating principles: (i) The details of the grain boundaries are irrelevant in the degradation process, and they only provide the initial nuclei for water phase-segregation. (ii) The supply of water molecules that drives the degradation forward are not provided via grain boundaries, but by water molecules readily diffusing through the bulk of the material. Leguy *et al.* attributed the homogeneous and isotropic progression of degradation to rapid transport of water molecules along the grain boundaries,⁹³ while we propose that the water

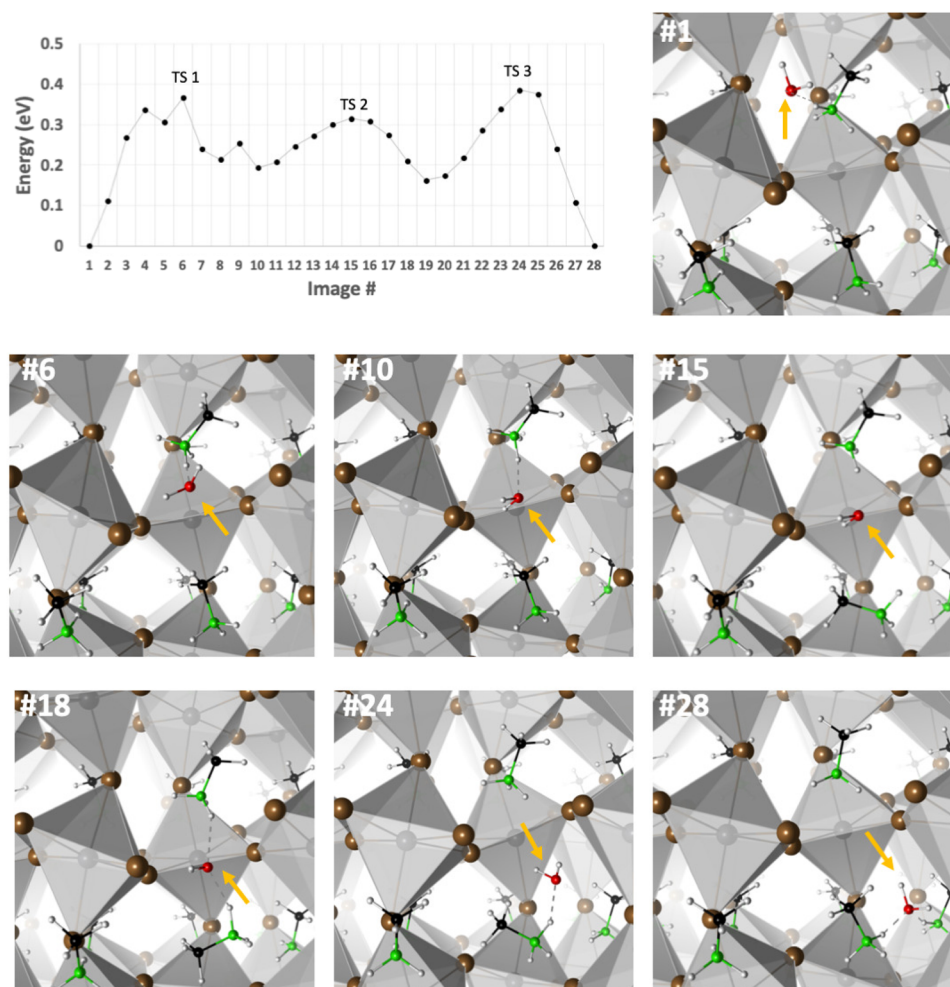


FIG. 11. Minimum-energy pathway for H_2O diffusion at low concentrations along the c axis. A few important images are shown, including the first TS image #6, the second TS image #15, and the third TS image #24. Color code is O (red), H (white), C (black), N (green), I (brown), and Pb (dark gray).

shuttling is done by the bulk of the MAPbI_3 rather than the grain boundaries. Here, the grain boundaries are only responsible for providing initial high-concentration water nuclei for phase segregation. As the degradation proceeds and the monohydrate phase propagates in-plane toward the grain center,¹²⁷ what used to be a grain boundary is now a monohydrate-perovskite interface. It is not guaranteed that such an interface-independent of local details of the sample keeps universal water permittivity characteristics. On the other hand, a bulk-driven water transport mechanism guarantees such universality.

It should be emphasized that the transformation of an over-stoichiometric super-hydrous state [$n\text{H}_2\text{O}\text{-MAPbI}_3$, ($n > 1$)] to a stoichiometric edge-sharing $\text{MAPbI}_3\cdot\text{H}_2\text{O}$ monohydrate locally leads to an excess of water molecules. These can then join the other over-stoichiometric regions and help catalyze the transformation of the rest of the sample into the edge-sharing phase.

We note that the super-hydrous state is a transient rather than a stable state, which acts as a bridge between the perovskite and edge-sharing structures. Thus, isolating and directly characterizing it as a stable phase might not be experimentally viable.

Nevertheless, this state has some unique characteristics that can be searched for as potentially experimentally testable fingerprints. This includes (a) the over-stoichiometric high concentration of H_2O molecules, (b) the aforementioned $\text{Pb}^{2+}\text{-H}_2\text{O}$ bonds, and (c) the volume expansion ($\sim 13\%$) relative to the perovskite phase and ($\sim 7\%$) relative to the edge-sharing monohydrate. In a real sample, depending on the local constitution and topography, the formation of the super-hydrous state might lead to a stress field in the interface with the rest of the material (either perovskite or edge-sharing). An effective encapsulation scheme or interfacing with a hard material, especially in the limit of smaller perovskite nanoparticles, can in fact penalize the super-hydrous state, since transformation to a higher volume state at higher pressure incurs a greater Gibbs free energy penalty. Studying the effect of external pressure on the super-hydrous state can be the subject of future work.

The super-hydrous bulk-degradation model can help shed light upon the experimental evidence regarding the role of heterostructure/heterojunctioning^{157,158} and the dimensionality engineering^{159–165} on the stability of the halide-perovskite-based

systems. Quan *et al.*¹⁶⁶ have studied the stability of a class of mixed-cation Ruddlesden-Popper (RP)^{167,168} quasi-2D perovskite films $[(\text{PEA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}]$, $1 < n < \infty$ and have found an improved stability for smaller values of n . In addition to (a) the larger concentration (per Pb) of hydrophobic CH groups on the long-chain cations¹⁶⁸ and (b) the thermodynamic arguments originally presented by Quan *et al.* based on DFT-based formation enthalpies,¹⁶⁶ one can rationalize the kinetics behind this stability via our bulk degradation model. Decreasing n effectively reduces the dimensionality of the system, suppresses the bulk-driven degradation mechanism, and improves the stability. A central idea in our model is the role of initial high concentration nuclei necessary for creation and expansion of the super-hydrous regions. Based on the notion of electrostatics-driven¹⁴⁴ water bonding mechanism developed in this work, such initial nuclei tend to form in regions possessing high density of under-coordinated Pb^{2+} cations which can create effective 3D bonding motifs for stabilization of initial H_2O networks (e.g., nano-droplets). The dimensionality engineering schemes (e.g., quasi-2D structures with smaller n) can help eliminate such regions. Additionally, in such RP quasi-2D structures, even if the density of defects in a layer is high enough to create a super-hydrous region and degradation, they do not propagate to other layers separated by hydrophobic long organic cations. This should be contrasted with the discussed case of continuous 3D hybrid perovskites. Heterojunctioning can also be used for defects' suppression of perovskite's interfaces. Additionally, as mentioned before, interfacing (via strong contacts with harder materials) can help the stability (especially of smaller halide perovskite particles) by restraining the lattice constants and penalizing the higher volume super-hydrous state. Heterostructuring can also physically seal off the perovskite sample from the inbound water molecules, similar in philosophy to the encapsulation schemes.^{169,170} Jana and Kim have recently shown such protective interfaces do not necessarily need to be made with foreign materials or molecules but by transformation of the peripheral layers of the halide perovskites [to $\text{Pb}(\text{OH})_2$ in their work].¹⁷¹ Therefore, an effective perovskite-based heterostructure can be potentially used in a relatively harsh aqueous electrochemical environment for efficient (photo)catalysis.^{172–175}

Finally, it is worthy to note that Walsh and co-workers have studied defect (specifically vacancies) chemistry in bulk hydrated perovskite MAPbI_3 with stoichiometric $\text{H}_2\text{O}:\text{MA}$ ratio $[n\text{H}_2\text{O}:\text{MAPbI}_3 (n = 1)]$.^{126,176} They studied the effect of water on vacancy formation energetics and enhancing vacancy-mediated ion migration. This is indeed an important theoretical venue in understanding the bulk water chemistry, yet our approach in this work was different in philosophy. We propose that the degradation through a super-hydrous state can proceed without the need of pre-existing vacancies and can take place in a perfect bulk MAPbI_3 single crystal (given the initial high water concentration nuclei). In this mechanism, aggregation of water molecules naturally distorts the structure and catalyzes the phase transformation. Nonetheless, our super-hydrous bulk-degradation model suggests that at grain boundaries the defect chemistry of halide perovskites becomes particularly important to help understand the (in)stability of these materials. Such a bulk-driven mechanism should also be contrasted with the recent surface-driven mechanism proposed by Fan *et al.* for the thermal degradation of MAPbI_3 at higher temperatures and in the absence of water.^{40,177}

E. Connection to other hybrid-perovskites

The chemical bonding analysis and the degradation model hereby presented were centered on MAPbI_3 as representative of the hybrid-perovskites class. Nevertheless, this is extendable to the larger halide perovskite family.^{178–185} A critical feature of the super-hydrous state is water binding with the inorganic cation (IC), which is originally located in a symmetric cage of the halide anions. Water binding to the inorganic backbone requires the mechanical distortion of the octahedron and breaking of this symmetry. The strength of the chemical bond between the IC and the halide has a determining role in dictating the energetics of this mechanical deformation, thus the relative favorability and energetics of the super-hydrous state. The relative sizes of the IC and the halide also dictate their bond length, which is a factor that dictates the local electrostatics that determines the ESP well, lone-pair polarization, and the strength of the H_2O –IC bond.¹⁴⁴ A possible direction for future research will be to study the periodic trends in the energetics of the super-hydrous state (as a measure of the material's stability) vs the combination of different IC and halides. It might also be possible that some simple descriptors can be found to map the combinations-space to the aforementioned energetics. In principle, the effect of changing the organic cation's type and the associated trends can also be understood based on differences in (a) direct electrostatic interaction with water, (b) stabilizing interaction with the (bare and distorted) inorganic octahedra, (c) interaction with the intercalated H_2O bound to the distorted octahedra [see the discussions in Fig. 4(e) and Sec. 6 of the [supplementary material](#)], and (d) changing the water diffusion barrier through the bulk material (as shown above, interaction between water and the organic cation plays a central role in the water diffusion process).

V. CONCLUSIONS

We discussed the fundamental underlying physics and chemistry behind water bonding in MAPbI_3 by extending concepts from the recent theory of lone-pair–surface bonds.¹⁴⁴ The low concentration bonding mode for water is a relatively strong electrostatic bond between the polarized water lone-pair (mostly HOMO) and the proton-like ammonium H of MA^+ . The important electrostatic role of the extra hole on MA^+ in the H_2O binding energy (BE) was discussed. This hole redistributes itself closer to H_2O to enhance its bonding. The possibility of Pb-bound modes for water adsorption was also discussed. Here, the PbI_6 octahedron must be broken to create the appropriate electrostatics for H_2O lone-pair bonding. Such a bonding mode is not the ground state for lower water concentrations, but as water concentration increases ($n = \text{H}_2\text{O}:\text{MA} > 1$), H_2O –Pb bonds readily form and structures with broken PbI_6 octahedra occur as ground states. The role of H_2O molecules in increasing the bandgap of water-intercalated phases was discussed. In under-stoichiometric concentrations ($n = \text{H}_2\text{O}:\text{MA} < 1$), bandgap change is led by mechanical effects leading to a smaller degree of connectivity in the system, while in the over-stoichiometric regime ($n = \text{H}_2\text{O}:\text{MA} > 1$), the water has a chemical effect in widening the bandgap of the system, mostly through the formation of covalent bonds with under-coordinated Pb^{2+} sites.

By calculating the concentration dependence of water BE in MAPbI_3 , we showed that the stoichiometric water intercalated

configuration is only a local energy maximum (in H_2O BE vs concentration space), i.e., the system would rather phase-segregate into low- and high-concentration regions. The high-water-concentration (wet) regions, which we call a super-hydrous state, are structures with expanded volume and broken PbI_6 octahedra, in which the corner-sharing MAPbI_3 perovskite structure is ready to re-arrange itself into the edge-sharing $\text{MAPbI}_3 \cdot \text{H}_2\text{O}$ monohydrate phase. This transient intermediate state gives the organic and inorganic components of MAPbI_3 enough freedom to re-arrange into the colorless edge-sharing phase. This colorless phase is a local thermodynamic sink, even more energetically favorable than water intercalation in very low concentrations. Thus, the system (water intercalated perovskite MAPbI_3) has a thermodynamic tendency to form such segregated hydration states and then degrade into the colorless monohydrate.

We find small and virtually isotropic diffusion barriers (≈ 0.4 eV) through bulk perovskite MAPbI_3 . Thus, one should perceive MAPbI_3 as a water-permeable structure that is readily filled with a small concentration of water molecules. These water molecules distort the inorganic-backbone (although not directly bonding with it at small concentrations) and through these distortions repel other H_2O molecules. Thus, water in low concentration renders the sample more hydrophobic. Only once the water concentration is significantly increased ($n = \text{H}_2\text{O}:\text{MA} > 1$), the water molecules and their associated distortions become cooperative and hydrophilic, leading to a local super-hydrous state, further disrupting and expanding the inorganic backbone upon joining additional itinerant H_2O molecules.

Our model of super-hydrous mediated bulk degradation can be used to rationalize some important experimental observations including the macroscopically homogeneous and isotropic degradation of perovskite MAPbI_3 into the colorless monohydrate in multi-grain samples, and the in-plane direction of degradation growth in a single MAPbI_3 grain.^{93,127,128} In such a model, the grain boundaries, which possess a large concentration of defects, are natural nuclei at which the initial high water concentration for phase segregation can occur and from which the degradation propagates. Passivation of grain boundaries and regions with high densities of defects can then lead to kinetically suppressing the formation of high-water-concentration nuclei and thus the degradation process.^{186–197} Another strategy is improving the stability through limiting the number of entering H_2O molecules that can easily travel through the bulk MAPbI_3 and find and expand the wet regions, using capping or encapsulation schemes,^{198–208} or 2D-3D (mixed-dimensional) hybrid systems.^{160,209–213} The 2D-3D scheme (similar to the quasi-2D and interfacing schemes) can also enhance the stability by defects' suppression.^{214–217} The role of surfaces on the (opto)electronic properties of hybrid perovskites has been previously investigated.²¹⁸ Based on our results, surfaces do not have a direct influence on the degradation mechanism. However, passivation of the whole surface area of the sample can lead to water insulation of the sample, thus indirectly helping the stability. Similar to the grain-boundaries surfaces can also host a large number of defects. Nevertheless, 3D bonding motifs can occur much easier in the defected grain boundaries as opposed to the defected surfaces, and the existence of such favorable binding matrices means that the degradation nucleates in grain boundaries (rather than surfaces) and propagates in-plane toward the center of the grains (upon

joining other phase-segregated H_2O molecules) as experimentally observed.¹²⁷

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for more details on the computational methods, convergence tests, and further electronic structure analyses.

ACKNOWLEDGMENTS

The authors thank Diomedes Saldana-Greco for help and advice during the early stages of this project. This work was supported by the Office of Naval Research, under Grant No. N00014-17-1-2574. R.N.K. acknowledges the support of Vagelos Integrated Program in Energy Research (VIPER) at the University of Pennsylvania.

REFERENCES

- N. J. Jeon, H. G. Lee, Y. C. Kim, J. Seo, J. H. Noh, J. Lee, and S. I. Seok, *J. Am. Chem. Soc.* **136**, 7837–7840 (2014).
- M. K. Assadi, S. Bakhoda, R. Saidur, and H. Hanaei, *Renewable Sustainable Energy Rev.* **81**, 2812–2822 (2018).
- Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, and J. Huang, *Science* **347**, 967 (2015).
- M. Abdi-Jalebi, M. Pazoki, B. Philippe, M. I. Dar, M. Alsari, A. Sadhanala, G. Divitini, R. Imani, S. Lilliu, J. Kullgren, H. Rensmo, M. Grätzel, and R. H. Friend, *ACS Nano* **12**, 7301–7311 (2018).
- S. Svanström, T. Jesper Jacobsson, T. Sloboda, E. Giangrisostomi, R. Ovsyanikov, H. Rensmo, and U. B. Cappel, *J. Mater. Chem. A* **6**, 22134–22144 (2018).
- P. K. Nayak, M. Sendner, B. Wenger, Z. Wang, K. Sharma, A. J. Ramadan, R. Lovrinčić, A. Pucci, P. K. Madhu, and H. J. Snaith, *J. Am. Chem. Soc.* **140**, 574–577 (2018).
- D. A. Egger, A. Bera, D. Cahen, G. Hodes, T. Kirchartz, L. Kronik, R. Lovrinčić, A. M. Rappe, D. R. Reichman, and O. Yaffe, *Adv. Mater.* **30**, 1800691 (2018).
- I. Spanopoulos, W. Ke, C. C. Stoumpos, E. C. Schueller, O. Y. Kontsevoi, R. Seshadri, and M. G. Kanatzidis, *J. Am. Chem. Soc.* **140**, 5728–5742 (2018).
- Y. Wang, T. Gould, J. F. Dobson, H. Zhang, H. Yang, X. Yao, and H. Zhao, *Phys. Chem. Chem. Phys.* **16**, 1424–1429 (2013).
- B. Cheng, T.-Y. Li, P.-C. Wei, J. Yin, K.-T. Ho, J. R. D. Retamal, O. F. Mohammed, and J.-H. He, *Nat. Commun.* **9**, 5196 (2018).
- Y. Ling, Z. Yuan, Y. Tian, X. Wang, J. C. Wang, Y. Xin, K. Hanson, B. Ma, and H. Gao, *Adv. Mater.* **28**, 305–311 (2016).
- Y. Lee, J. Kwon, E. Hwang, C.-H. Ra, W. J. Yoo, J.-H. Ahn, J. H. Park, and J. H. Cho, *Adv. Mater.* **27**, 41–46 (2015).
- L. Dou, Y. M. Yang, J. You, Z. Hong, W.-H. Chang, G. Li, and Y. Yang, *Nat. Commun.* **5**, 5404 (2014).
- Y. Fang, Q. Dong, Y. Shao, Y. Yuan, and J. Huang, *Nat. Photonics* **9**, 679–686 (2015).
- C. Ji, P. Wang, Z. Wu, Z. Sun, L. Li, J. Zhang, W. Hu, M. Hong, and J. Luo, *Adv. Funct. Mater.* **28**, 1705467 (2018).
- P. Wangyang, C. Gong, G. Rao, K. Hu, X. Wang, C. Yan, L. Dai, C. Wu, and J. Xiong, *Adv. Opt. Mater.* **6**, 1701302 (2018).
- Z. Xiao, L. Zhao, N. L. Tran, Y. L. Lin, S. H. Silver, R. A. Kerner, N. Yao, A. Kahn, G. D. Scholes, and B. P. Rand, *Nano Lett.* **17**, 6863–6869 (2017).
- B. Turedi, K. J. Lee, I. Dursun, B. Alamer, Z. Wu, E. Alarousu, O. F. Mohammed, N. Cho, and O. M. Bakr, *J. Phys. Chem. C* **122**, 14128–14134 (2018).
- L. Ji, H.-Y. Hsu, J. C. Lee, A. J. Bard, and E. T. Yu, *Nano Lett.* **18**, 994–1000 (2018).
- S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, and H. J. Snaith, *Science* **342**, 341–344 (2013).

- ²¹T. Abraha Berhe, W.-N. Su, C.-H. Chen, C.-J. Pan, J.-H. Cheng, H.-M. Chen, M.-C. Tsai, L.-Y. Chen, A. Aregahegn Dubale, and B.-J. Hwang, *Energy Environ. Sci.* **9**, 323–356 (2016).
- ²²J. You, Z. Hong, Y. M. Yang, Q. Chen, M. Cai, T.-B. Song, C.-C. Chen, S. Lu, Y. Liu, H. Zhou, and Y. Yang, *ACS Nano* **8**, 1674–1680 (2014).
- ²³D. Pérez-del Rey, D. Forgács, E. M. Hutter, T. J. Savenije, D. Nordlund, P. Schulz, J. J. Berry, M. Sessolo, and H. J. Bolink, *Adv. Mater.* **28**, 9839–9845 (2016).
- ²⁴Y. Bi, E. M. Hutter, Y. Fang, Q. Dong, J. Huang, and T. J. Savenije, *J. Phys. Chem. Lett.* **7**, 923–928 (2016).
- ²⁵J. Jean, J. Xiao, R. Nick, N. Moody, M. Nasilowski, M. Bawendi, and V. Bulović, *Energy Environ. Sci.* **11**, 2295–2305 (2018).
- ²⁶F. Zheng, L. Z. Tan, S. Liu, and A. M. Rappe, *Nano Lett.* **15**, 7794–7800 (2015).
- ²⁷C. C. Stoumpos, C. D. Malliakas, and M. G. Kanatzidis, *Inorg. Chem.* **52**, 9019–9038 (2013).
- ²⁸J. Ma and L.-W. Wang, *Nano Lett.* **17**, 3646–3654 (2017).
- ²⁹J. Berry *et al.*, *Adv. Mater.* **27**, 5102–5112 (2015).
- ³⁰A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, *J. Am. Chem. Soc.* **131**, 6050–6051 (2009).
- ³¹A. B. Djurišić, F. Z. Liu, H. W. Tam, M. K. Wong, A. Ng, C. Surya, W. Chen, and Z. B. He, *Prog. Quantum Electron.* **53**, 1–37 (2017).
- ³²X. Zhou, J. Jankowska, H. Dong, and O. V. Prezhdo, *J. Energy Chem.* **27**, 637–649 (2018).
- ³³M. Moniruddin, B. Ilyassov, X. Zhao, E. Smith, T. Serikov, N. Ibrayev, R. Asmatulu, and N. Nuraje, *Mater. Today Energy* **7**, 246–259 (2018).
- ³⁴Q. V. Le, H. W. Jang, and S. Y. Kim, *Small Methods* **2**, 1700419 (2018).
- ³⁵M. I. H. Ansari, A. Qurashi, and M. K. Nazeeruddin, *J. Photochem. Photobiol., C* **35**, 1–24 (2018).
- ³⁶M. Saliba, M. Stollerfoht, C. M. Wolff, D. Neher, and A. Abate, *Joule* **2**, 1019–1024 (2018).
- ³⁷Ç. Odabaşı and R. Yıldırım, *Nano Energy* **56**, 770–791 (2019).
- ³⁸J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfhaarde, and A. Walsh, *Nano Lett.* **14**, 2584–2590 (2014).
- ³⁹C. Quarti, G. Grancini, E. Mosconi, P. Bruno, J. M. Ball, M. M. Lee, H. J. Snaith, A. Petrozza, and F. De Angelis, *J. Phys. Chem. Lett.* **5**, 279–284 (2014).
- ⁴⁰Z. Fan, H. Xiao, Y. Wang, Z. Zhao, Z. Lin, H.-C. Cheng, S.-J. Lee, G. Wang, Z. Feng, W. A. Goddard, Y. Huang, and X. Duan, *Joule* **1**, 548–562 (2017).
- ⁴¹N. M. Rahman, M. Adnan, D. Adhikary, M. Islam, and M. K. Alam, *Comput. Mater. Sci.* **150**, 439–447 (2018).
- ⁴²J. Li, J. Järvi, and P. Rinke, *Phys. Rev. B* **98**, 045201 (2018).
- ⁴³J.-H. Lee, Z. Deng, N. C. Bristowe, P. D. Bristowe, and A. K. Cheetham, *J. Mater. Chem. C* **6**, 12252–12259 (2018).
- ⁴⁴P. Umari, E. Mosconi, and F. De Angelis, *Sci. Rep.* **4**, 4467 (2014).
- ⁴⁵D. Shi *et al.*, *Science* **347**, 519–522 (2015).
- ⁴⁶S. Liu, F. Zheng, N. Z. Koocher, H. Takenaka, F. Wang, and A. M. Rappe, *J. Phys. Chem. Lett.* **6**, 693–699 (2015).
- ⁴⁷S. De Wolf, J. Holovsky, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum, and C. Ballif, *J. Phys. Chem. Lett.* **5**, 1035–1039 (2014).
- ⁴⁸H. Choi, J. Jeong, H.-B. Kim, S. Kim, B. Walker, G.-H. Kim, and J. Y. Kim, *Nano Energy* **7**, 80–85 (2014).
- ⁴⁹D. A. Egger, A. M. Rappe, and L. Kronik, *Acc. Chem. Res.* **49**, 573–581 (2016).
- ⁵⁰B. Chen, X. Zheng, M. Yang, Y. Zhou, S. Kundu, J. Shi, K. Zhu, and S. Priya, *Nano Energy* **13**, 582–591 (2015).
- ⁵¹S. Liu, F. Zheng, I. Grinberg, and A. M. Rappe, *J. Phys. Chem. Lett.* **7**, 1460–1465 (2016).
- ⁵²J. Huang, Y. Yuan, Y. Shao, and Y. Yan, *Nat. Rev. Mater.* **2**, 17042 (2017).
- ⁵³S. T. Birkhold, H. Hu, P. T. Höger, K. K. Wong, P. Rieder, A. Baumann, and L. Schmidt-Mende, *J. Phys. Chem. C* **122**, 12140–12147 (2018).
- ⁵⁴N. P. Gallop, O. Selig, G. Giubertoni, H. J. Bakker, Y. L. A. Rezus, J. M. Frost, T. L. C. Jansen, R. Lovrincic, and A. A. Bakulin, *J. Phys. Chem. Lett.* **9**, 5987–5997 (2018).
- ⁵⁵J. Jankowska and O. V. Prezhdo, *J. Phys. Chem. Lett.* **8**, 812–818 (2017).
- ⁵⁶G. P. Nagabhushana, R. Shivaramaiah, and A. Navrotsky, *Proc. Natl. Acad. Sci. U. S. A.* **113**, 7717–7721 (2016).
- ⁵⁷A. Cicciooli and A. Latini, *J. Phys. Chem. Lett.* **9**, 3756–3765 (2018).
- ⁵⁸B. Brunetti, C. Cavallo, A. Cicciooli, G. Gigli, and A. Latini, *Sci. Rep.* **6**, 31896 (2016).
- ⁵⁹A. Latini, G. Gigli, and A. Cicciooli, *Sustainable Energy Fuels* **1**, 1351–1357 (2017).
- ⁶⁰Y. Xue, Y. Shan, and H. Xu, *J. Chem. Phys.* **147**, 124702 (2017).
- ⁶¹Y.-Y. Zhang, S. Chen, P. Xu, H. Xiang, X.-G. Gong, A. Walsh, and S.-H. Wei, *Chin. Phys. Lett.* **35**, 036104 (2018).
- ⁶²B. Conings, J. Drijkoningen, N. Gauquelin, A. Babayigit, J. D’Haen, L. D’Oleslaeger, A. Ethirajan, J. Verbeeck, J. Manca, E. Mosconi, F. D. Angelis, and H.-G. Boyen, *Adv. Energy Mater.* **5**, 1500477 (2015).
- ⁶³W. Wei and Y. H. Hu, *Int. J. Energy Res.* **41**, 1063–1069 (2017).
- ⁶⁴J. A. McLeod and L. Liu, *J. Phys. Chem. Lett.* **9**, 2411–2417 (2018).
- ⁶⁵J. Yang, Z. Yuan, X. Liu, S. Braun, Y. Li, J. Tang, F. Gao, C. Duan, M. Fahlman, and Q. Bao, *ACS Appl. Mater. Interfaces* **10**, 16225–16230 (2018).
- ⁶⁶F. U. Kosasih and C. Ducati, *Nano Energy* **47**, 243–256 (2018).
- ⁶⁷N. Aristidou, C. Eames, M. S. Islam, and S. A. Haque, *J. Mater. Chem. A* **5**, 25469–25475 (2017).
- ⁶⁸E. Smecca, Y. Numata, I. Deretzi, G. Pellegrino, S. Boninelli, T. Miyasaka, A. L. Magna, and A. Alberti, *Phys. Chem. Chem. Phys.* **18**, 13413–13422 (2016).
- ⁶⁹M. I. Saidaminov, J. Kim, A. Jain, R. Quintero-Bermudez, H. Tan, G. Long, F. Tan, A. Johnston, Y. Zhao, O. Voznyy, and E. H. Sargent, *Nat. Energy* **3**, 648 (2018).
- ⁷⁰G. E. Eperon, S. N. Habisreutinger, T. Leijtens, B. J. Bruijns, J. J. van Franeker, D. W. deQuilettes, S. Pathak, R. J. Sutton, G. Grancini, D. S. Ginger, R. A. J. Janssen, A. Petrozza, and H. J. Snaith, *ACS Nano* **9**, 9380–9393 (2015).
- ⁷¹K. K. Bass, R. E. McAnally, S. Zhou, P. I. Djurovich, M. E. Thompson, and B. C. Melot, *Chem. Commun.* **50**, 15819–15822 (2014).
- ⁷²H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, and Y. Yang, *Science* **345**, 542–546 (2014).
- ⁷³J. Li, A. Dobrovolsky, A. Merdasa, E. L. Unger, and I. G. Scheblykin, *ACS Omega* **3**, 14494–14502 (2018).
- ⁷⁴J. Huang, S. Tan, P. D. Lund, and H. Zhou, *Energy Environ. Sci.* **10**, 2284–2311 (2017).
- ⁷⁵L. Contreras-Bernal, C. Aranda, M. Valles-Pelarda, T. T. Ngo, S. Ramos-Terrón, J. J. Gallardo, J. Navas, A. Guerrero, I. Mora-Seró, J. Idigoras, and J. A. Anta, *J. Phys. Chem. C* **122**, 5341–5348 (2018).
- ⁷⁶M. L. Petrus, Y. Hu, D. Moia, P. Calado, A. M. A. Leguy, P. R. F. Barnes, and P. Docampo, *ChemSusChem* **9**, 2699–2707 (2016).
- ⁷⁷C.-H. Chiang and C.-G. Wu, *ACS Nano* **12**, 10355–10364 (2018).
- ⁷⁸S. Yang, Y. Wang, P. Liu, Y.-B. Cheng, H. J. Zhao, and H. G. Yang, *Nat. Energy* **1**, 15016 (2016).
- ⁷⁹Q. Lv, W. He, Z. Lian, J. Ding, Q. Li, and Q. Yan, *CrystEngComm* **19**, 901–904 (2017).
- ⁸⁰T. Y. Wen, S. Yang, P. F. Liu, L. J. Tang, H. W. Qiao, X. Chen, X. H. Yang, Y. Hou, and H. G. Yang, *Adv. Energy Mater.* **8**, 1703143 (2018).
- ⁸¹P. Holzhey, P. Yadav, S.-H. Turren-Cruz, M. Grätzel, A. Hagfeldt, and M. Saliba, “A chain is as strong as its weakest link—Stability study of MAPbI₃ under light and temperature,” *Mater. Today* (published online).
- ⁸²J. Wei, F. Huang, S. Wang, L. Zhou, P. Jin, Y. Xin, Z. Cai, Z. Yin, Q. Pang, and J. Z. Zhang, *ChemNanoMat* **4**, 649–655 (2018).
- ⁸³C. Law, L. Miseikis, S. Dimitrov, P. Shukya-Tuladhar, X. Li, P. R. F. Barnes, J. Durrant, and B. C. O’Regan, *Adv. Mater.* **26**, 6268–6273 (2014).
- ⁸⁴B. Li, M. Wang, R. Subair, G. Cao, and J. Tian, *J. Phys. Chem. C* **122**, 25260–25267 (2018).
- ⁸⁵M. Wong-Stringer, O. S. Game, J. A. Smith, T. J. Routledge, B. A. Alqurashy, B. G. Freestone, A. J. Parnell, N. Vaenas, V. Kumar, M. O. A. Alawad, A. Iraqi, C. Rodenburg, and D. G. Lidzey, *Adv. Energy Mater.* **8**, 1801234 (2018).
- ⁸⁶J. Idigoras, F. J. Aparicio, L. Contreras-Bernal, S. Ramos-Terrón, M. Alcaire, J. R. Sánchez-Valencia, A. Borrás, Á. Barranco, and J. A. Anta, *ACS Appl. Mater. Interfaces* **10**, 11587–11594 (2018).
- ⁸⁷C. C. Boyd, R. Cheacharoen, T. Leijtens, and M. D. McGehee, *Chem. Rev.* **119**, 3418 (2018).

- ⁸⁸Z. Wang, Q. Ou, Y. Zhang, Q. Zhang, H. Y. Hoh, and Q. Bao, *ACS Appl. Mater. Interfaces* **10**, 24258–24265 (2018).
- ⁸⁹Y. Han, S. Meyer, Y. Dkhissi, K. Weber, J. M. Pringle, U. Bach, L. Spiccia, and Y.-B. Cheng, *J. Mater. Chem. A* **3**, 8139–8147 (2015).
- ⁹⁰R. K. Misra, S. Aharon, B. Li, D. Mogilyansky, I. Visoly-Fisher, L. Etgar, and E. A. Katz, *J. Phys. Chem. Lett.* **6**, 326–330 (2015).
- ⁹¹N. Tripathi, M. Yanagida, Y. Shirai, T. Masuda, L. Han, and K. Miyano, *J. Mater. Chem. A* **3**, 12081–12088 (2015).
- ⁹²D. B. Khadka, Y. Shirai, M. Yanagida, and K. Miyano, *J. Mater. Chem. C* **6**, 162–170 (2018).
- ⁹³A. M. A. Leguy, Y. Hu, M. Campoy-Quiles, M. I. Alonso, O. J. Weber, P. Azarhoosh, M. van Schilfgaarde, M. T. Weller, T. Bein, J. Nelson, P. Docampo, and P. R. F. Barnes, *Chem. Mater.* **27**, 3397–3407 (2015).
- ⁹⁴Z. Zhu *et al.*, *Chem. Mater.* **28**, 7385–7393 (2016).
- ⁹⁵H.-S. Kim, J.-Y. Seo, and N.-G. Park, *ChemSusChem* **9**, 2528–2540 (2016).
- ⁹⁶J. Yang, B. D. Siempelkamp, D. Liu, and T. L. Kelly, *ACS Nano* **9**, 1955–1963 (2015).
- ⁹⁷A. M. Askar, G. M. Bernard, B. Wiltshire, K. Shankar, and V. K. Michaelis, *J. Phys. Chem. C* **121**, 1013–1024 (2017).
- ⁹⁸C. Wang and Y. Gao, *J. Phys. Chem. Lett.* **9**, 4657–4666 (2018).
- ⁹⁹F. Lang, O. Shargaieva, V. V. Brus, H. C. Neitzert, J. Rappich, and N. H. Nickel, *Adv. Mater.* **30**, 1702905 (2018).
- ¹⁰⁰L. Zhang, M.-G. Ju, and W. Liang, *Phys. Chem. Chem. Phys.* **18**, 23174–23183 (2016).
- ¹⁰¹G. Grancini, V. D’Innocenzo, E. R. Dohner, N. Martino, A. R. S. Kandada, E. Mosconi, F. D. Angelis, H. I. Karunadasa, E. T. Hoke, and A. Petrozza, *Chem. Sci.* **6**, 7305–7310 (2015).
- ¹⁰²I. Deretzis, E. Smecca, G. Mannino, A. La Magna, T. Miyasaka, and A. Alberti, *J. Phys. Chem. Lett.* **9**, 3000–3007 (2018).
- ¹⁰³N. Calisi, S. Caporali, A. Milanesi, M. Innocenti, E. Salviati, and U. Bardi, *Top. Catal.* **61**, 1201–1208 (2018).
- ¹⁰⁴M. Hada, Y. Hasegawa, R. Nagaoka, T. Miyake, U. Abdullaev, H. Ota, T. Nishikawa, Y. Yamashita, and Y. Hayashi, *Jpn. J. Appl. Phys., Part 1* **57**, 028001 (2018).
- ¹⁰⁵Z. Song, N. Shrestha, S. C. Watthage, G. K. Liyanage, Z. S. Almutawah, R. H. Ahangharnejhad, A. B. Phillips, R. J. Ellingson, and M. J. Heben, *J. Phys. Chem. Lett.* **9**, 6312–6320 (2018).
- ¹⁰⁶B. Akbali, G. Topcu, T. Guner, M. Ozcan, M. M. Demir, and H. Sahin, *Phys. Rev. Mater.* **2**, 034601 (2018).
- ¹⁰⁷Y. Guo, C. Li, X. Li, Y. Niu, S. Hou, and F. Wang, *J. Phys. Chem. C* **121**, 12711–12717 (2017).
- ¹⁰⁸L. Zhang and P. H.-L. Sit, *J. Mater. Chem. A* **5**, 23976–23986 (2017).
- ¹⁰⁹L. Zhang and P. H.-L. Sit, *J. Mater. Chem. A* **5**, 9042–9049 (2017).
- ¹¹⁰Y. Guo, C. Li, Y. Xue, C. Geng, and D. Tian, *Mater. Res. Express* **5**, 026203 (2018).
- ¹¹¹L. Zhang and P. H.-L. Sit, *J. Phys. Chem. C* **119**, 22370–22378 (2015).
- ¹¹²C.-L. Yao, J.-C. Li, W. Gao, and Q. Jiang, *J. Phys. Chem. Lett.* **9**, 5386–5391 (2018).
- ¹¹³C. Peng, J. Chen, H. Wang, and P. Hu, *J. Phys. Chem. C* **122**, 27340–27349 (2018).
- ¹¹⁴L. Zhang, L. Xu, Q. Li, J. Su, and J. Li, *Sol. Energy Mater. Sol. Cells* **186**, 349–355 (2018).
- ¹¹⁵L. Zhang, X. Liu, J. Li, and S. McKechnie, *Sol. Energy Mater. Sol. Cells* **175**, 1–19 (2018).
- ¹¹⁶C.-J. Tong, W. Geng, Z.-K. Tang, C.-Y. Yam, X.-L. Fan, J. Liu, W.-M. Lau, and L.-M. Liu, *J. Phys. Chem. Lett.* **6**, 3289–3295 (2015).
- ¹¹⁷Y.-B. Lu, C. Guan, H. Sun, W.-Y. Cong, H. Yang, and P. Zhang, *J. Phys. Chem. C* **122**, 11862–11869 (2018).
- ¹¹⁸W. Hao, X. Chen, and S. Li, *J. Phys. Chem. C* **120**, 28448–28455 (2016).
- ¹¹⁹P.-P. Sun, W.-J. Chi, and Z.-S. Li, *Phys. Chem. Chem. Phys.* **18**, 24526–24536 (2016).
- ¹²⁰S. Lu, Q. Zhou, Y. Ouyang, Y. Guo, Q. Li, and J. Wang, *Nat. Commun.* **9**, 3405 (2018).
- ¹²¹Y. Liu, K. Palotas, X. Yuan, T. Hou, H. Lin, Y. Li, and S.-T. Lee, *ACS Nano* **11**, 2060–2065 (2017).
- ¹²²N. Z. Koocher, D. Saldana-Greco, F. Wang, S. Liu, and A. M. Rappe, *J. Phys. Chem. Lett.* **6**, 4371–4378 (2015).
- ¹²³E. Mosconi, J. M. Azpiroz, and F. De Angelis, *Chem. Mater.* **27**, 4885–4892 (2015).
- ¹²⁴C. Caddeo, M. I. Saba, S. Meloni, A. Filippetti, and A. Mattoni, *ACS Nano* **11**, 9183–9190 (2017).
- ¹²⁵G. N. Hall, M. Stuckelberger, T. Nietzold, J. Hartman, J.-S. Park, J. Werner, B. Niesen, M. L. Cummings, V. Rose, C. Ballif, M. K. Chan, D. P. Fenning, and M. I. Bertoni, *J. Phys. Chem. C* **121**, 25659–25665 (2017).
- ¹²⁶U.-G. Jong, C.-J. Yu, G.-C. Ri, A. P. McMahon, N. M. Harrison, P. R. F. Barnes, and A. Walsh, *J. Mater. Chem. A* **6**, 1067–1074 (2018).
- ¹²⁷Q. Wang, B. Chen, Y. Liu, Y. Deng, Y. Bai, Q. Dong, and J. Huang, *Energy Environ. Sci.* **10**, 516–522 (2017).
- ¹²⁸T. Niu, J. Lu, R. Munir, J. Li, D. Barrit, X. Zhang, H. Hu, Z. Yang, A. Amassian, K. Zhao, and S. F. Liu, *Adv. Mater.* **30**, 1706576 (2018).
- ¹²⁹W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133–A1138 (1965).
- ¹³⁰P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864–B871 (1964).
- ¹³¹P. Giannozzi *et al.*, *J. Phys.: Condens. Matter* **30**, 395502 (2009).
- ¹³²K. F. Garrity, J. W. Bennett, K. M. Rabe, and D. Vanderbilt, *Comput. Mater. Sci.* **81**, 446–452 (2014).
- ¹³³J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- ¹³⁴S. Grimme, *J. Comput. Chem.* **25**, 1463–1473 (2004).
- ¹³⁵S. Grimme, *J. Comput. Chem.* **27**, 1787–1799 (2006).
- ¹³⁶G. Henkelman, B. P. Uberuaga, and H. Jónsson, *J. Chem. Phys.* **113**, 9901–9904 (2000).
- ¹³⁷G. Henkelman and H. Jónsson, *J. Chem. Phys.* **113**, 9978–9985 (2000).
- ¹³⁸G. Mills and H. Jónsson, *Phys. Rev. Lett.* **72**, 1124–1127 (1994).
- ¹³⁹G. Mills, H. Jónsson, and G. K. Schenter, *Surf. Sci.* **324**, 305–337 (1995).
- ¹⁴⁰R. D. Hoehn, J. S. Francisco, S. Kais, and A. Kachmar, *Sci. Rep.* **9**, 668 (2019).
- ¹⁴¹G. J. Martyna and M. E. Tuckerman, *J. Chem. Phys.* **110**, 2810–2821 (1999).
- ¹⁴²G. Henkelman, A. Arnaldsson, and H. Jónsson, *Comput. Mater. Sci.* **36**, 354–360 (2006).
- ¹⁴³E. Sanville, S. D. Kenny, R. Smith, and G. Henkelman, *J. Comput. Chem.* **28**, 899–908 (2007).
- ¹⁴⁴A. Kakekhani, L. T. Roling, A. Kulkarni, A. A. Latimer, H. Abroshan, J. Schumann, H. Aljama, S. Siahrostami, S. Ismail-Beigi, F. Abild-Pedersen, and J. K. Nørskov, *Inorg. Chem.* **57**, 7222–7238 (2018).
- ¹⁴⁵D. Silber, P. M. Kowalski, F. Traeger, M. Buchholz, F. Bebensee, B. Meyer, and C. Wöll, *Nat. Commun.* **7**, 12888 (2016).
- ¹⁴⁶V. A. Ranea, W. F. Schneider, and I. Carmichael, *Surf. Sci.* **602**, 268–275 (2008).
- ¹⁴⁷T. Zhang, X. Meng, Y. Bai, S. Xiao, C. Hu, Y. Yang, H. Chen, and S. Yang, *J. Mater. Chem. A* **5**, 1103–1111 (2017).
- ¹⁴⁸D. Li, J. Shi, Y. Xu, Y. Luo, H. Wu, and Q. Meng, *Natl. Sci. Rev.* **5**, 559–576 (2018).
- ¹⁴⁹F.-X. Coudert, A. H. Fuchs, and A. V. Neimark, *Phys. Chem. Chem. Phys.* **16**, 4394–4395 (2014).
- ¹⁵⁰Z.-K. Tang, Y.-N. Zhu, Z.-F. Xu, and L.-M. Liu, *Phys. Chem. Chem. Phys.* **19**, 14955–14960 (2017).
- ¹⁵¹R. Prasanna, A. Gold-Parker, T. Leijtens, B. Conings, A. Babayigit, H.-G. Boyen, M. F. Toney, and M. D. McGehee, *J. Am. Chem. Soc.* **139**, 11117–11124 (2017).
- ¹⁵²Z. Xiao, W. Meng, J. Wang, D. B. Mitzi, and Y. Yan, *Mater. Horiz.* **4**, 206–216 (2017).
- ¹⁵³Z. Xiao, Y. Zhou, H. Hosono, T. Kamiya, and N. P. Padture, *Chem.–Eur. J.* **24**, 2305–2316 (2018).
- ¹⁵⁴C. Müller, T. Glaser, M. Plogmeyer, M. Sendner, S. Döring, A. A. Bakulin, C. Brzuska, R. Scheer, M. S. Pshenichnikov, W. Kowalsky, A. Pucci, and R. Lovrinčić, *Chem. Mater.* **27**, 7835–7841 (2015).
- ¹⁵⁵J. Schlipf, L. Bieffmann, L. Oesinghaus, E. Berger, E. Metwalli, J. A. Lercher, L. Porcar, and P. Müller-Buschbaum, *J. Phys. Chem. Lett.* **9**, 2015–2021 (2018).

- ¹⁵⁶J. S. Yun, J. Kim, T. Young, R. J. Patterson, D. Kim, J. Seidel, S. Lim, M. A. Green, S. Huang, and A. Ho-Baillie, *Adv. Funct. Mater.* **28**, 1705363 (2018).
- ¹⁵⁷A. M. Al-Amri, B. Cheng, and J. He, *IEEE Trans. Nanotechnol.* **18**, 1–12 (2019).
- ¹⁵⁸Y. Zhang, W. Xu, X. Xu, J. Cai, W. Yang, and X. Fang, *J. Phys. Chem. Lett.* **10**, 836–841 (2019).
- ¹⁵⁹C. Lan, Z. Zhou, R. Wei, and J. C. Ho, *Mater. Today Energy* **11**, 61–82 (2019).
- ¹⁶⁰P. Gao, A. R. B. M. Yusoff, and M. K. Nazeeruddin, *Nat. Commun.* **9**, 5028 (2018).
- ¹⁶¹Q. Fu, X. Tang, B. Huang, T. Hu, L. Tan, L. Chen, and Y. Chen, *Adv. Sci.* **5**, 1700387 (2018).
- ¹⁶²I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee, and H. I. Karunadasa, *Angew. Chem.* **126**, 11414–11417 (2014).
- ¹⁶³F. Li, Y. Pei, F. Xiao, T. Zeng, Z. Yang, J. Xu, J. Sun, B. Peng, and M. Liu, *Nanoscale* **10**, 6318–6322 (2018).
- ¹⁶⁴A. Shpatz Dayan, B.-E. Cohen, S. Aharon, C. Tenailleau, M. Wierzbowska, and L. Etgar, *Chem. Mater.* **30**, 8017–8024 (2018).
- ¹⁶⁵J. W. Lim, H. Wang, C. H. Choi, H. Kwon, L. N. Quan, W.-T. Park, Y.-Y. Noh, and D. H. Kim, *Nano Energy* **57**, 761–770 (2019).
- ¹⁶⁶L. N. Quan, M. Yuan, R. Comin, O. Voznyy, E. M. Beauregard, S. Hoogland, A. Buin, A. R. Kirmani, K. Zhao, A. Amassian, D. H. Kim, and E. H. Sargent, *J. Am. Chem. Soc.* **138**, 2649–2655 (2016).
- ¹⁶⁷F. Xu, T. Zhang, G. Li, and Y. Zhao, *J. Mater. Chem. A* **5**, 11450–11461 (2017).
- ¹⁶⁸Y. Chen, Y. Sun, J. Peng, J. Tang, K. Zheng, and Z. Liang, *Adv. Mater.* **30**, 1703487 (2018).
- ¹⁶⁹I. S. Kim, D. H. Cao, D. B. Buchholz, J. D. Emery, O. K. Farha, J. T. Hupp, M. G. Kanatzidis, and A. B. F. Martinson, *Nano Lett.* **16**, 7786–7790 (2016).
- ¹⁷⁰J. You, L. Meng, T.-B. Song, T.-F. Guo, Y. M. Yang, W.-H. Chang, Z. Hong, H. Chen, H. Zhou, Q. Chen, Y. Liu, N. De Marco, and Y. Yang, *Nat. Nanotechnol.* **11**, 75–81 (2016).
- ¹⁷¹A. Jana and K. S. Kim, *ACE Energy Lett.* **3**, 2120–2126 (2018).
- ¹⁷²I. S. Kim, M. J. Pellin, and A. B. F. Martinson, *ACE Energy Lett.* **4**, 293–298 (2019).
- ¹⁷³H. Zhang, Z. Yang, W. Yu, H. Wang, W. Ma, X. Zong, and C. Li, *Adv. Energy Mater.* **8**, 1800795 (2018).
- ¹⁷⁴P. Da, M. Cha, L. Sun, Y. Wu, Z.-S. Wang, and G. Zheng, *Nano Lett.* **15**, 3452–3457 (2015).
- ¹⁷⁵S. Nam, C. T. K. Mai, and I. Oh, *ACS Appl. Mater. Interfaces* **10**, 14659–14664 (2018).
- ¹⁷⁶Y.-H. Kye, C.-J. Yu, U.-G. Jong, Y. Chen, and A. Walsh, *J. Phys. Chem. Lett.* **9**, 2196–2201 (2018).
- ¹⁷⁷B. R. Sutherland, *Joule* **1**, 423–424 (2017).
- ¹⁷⁸S. Dastidar, C. J. Hawley, A. D. Dillon, A. D. Gutierrez-Perez, J. E. Spanier, and A. T. Fafarman, *J. Phys. Chem. Lett.* **8**, 1278–1282 (2017).
- ¹⁷⁹G. A. Elbaz, D. B. Straus, O. E. Semonin, T. D. Hull, D. W. Paley, P. Kim, J. S. Owen, C. R. Kagan, and X. Roy, *Nano Lett.* **17**, 1727–1732 (2017).
- ¹⁸⁰Y. He, S.-Q. Wang, X.-X. Xue, L. Zhang, K. Chen, W.-X. Zhou, and Y. Feng, *J. Phys.: Condens. Matter* **30**, 355501 (2018).
- ¹⁸¹W.-Q. Liao, Y. Zhang, C.-L. Hu, J.-G. Mao, H.-Y. Ye, P.-F. Li, S. D. Huang, and R.-G. Xiong, *Nat. Commun.* **6**, 7338 (2015).
- ¹⁸²S. D. Stranks and H. J. Snaith, *Nat. Nanotechnol.* **10**, 391–402 (2015).
- ¹⁸³W. Li, Z. Wang, F. Deschler, S. Gao, R. H. Friend, and A. K. Cheetham, *Nat. Rev. Mater.* **2**, 16099 (2017).
- ¹⁸⁴T. Yoon, G.-H. Kim, C. W. Myung, S. Kajal, J. Jeong, J. W. Kim, J. Y. Kim, and K. S. Kim, *ACS Appl. Energy Mater.* **1**, 5865–5871 (2018).
- ¹⁸⁵J. Rodríguez-Romero, B. C. Hames, P. Galar, A. Fakharuddin, I. Suarez, L. Schmidt-Mende, J. P. Martínez-Pastor, A. Douhal, I. Mora-Seró, and E. M. Barea, *Phys. Chem. Chem. Phys.* **20**, 30189–30199 (2018).
- ¹⁸⁶B. Li, C. Fei, K. Zheng, X. Qu, T. Pullerits, G. Cao, and J. Tian, *J. Mater. Chem. A* **4**, 17018–17024 (2016).
- ¹⁸⁷J. He, C.-F. Ng, K. Young Wong, W. Liu, and T. Chen, *ChemPlusChem* **81**, 1292–1298 (2016).
- ¹⁸⁸X. Li, M. Ibrahim Dar, C. Yi, J. Luo, M. Tschumi, S. M. Zakeeruddin, M. K. Nazeeruddin, H. Han, and M. Grätzel, *Nat. Chem.* **7**, 703–711 (2015).
- ¹⁸⁹B. Li, V. Ferguson, S. R. P. Silva, and W. Zhang, *Adv. Mater. Interfaces* **5**, 1800326 (2018).
- ¹⁹⁰D. S. Lee, J. S. Yun, J. Kim, A. M. Soufiani, S. Chen, Y. Cho, X. Deng, J. Seidel, S. Lim, S. Huang, and A. W. Y. Ho-Baillie, *ACE Energy Lett.* **3**, 647–654 (2018).
- ¹⁹¹A. Gomez, S. Sanchez, M. Campoy-Quiles, and A. Abate, *Nano Energy* **45**, 94–100 (2018).
- ¹⁹²S.-G. Kim, J. Chen, J.-Y. Seo, D.-H. Kang, and N.-G. Park, *ACS Appl. Mater. Interfaces* **10**, 25372–25383 (2018).
- ¹⁹³G. Giorgi, K. Yamashita, and H. Segawa, *Phys. Chem. Chem. Phys.* **20**, 11183–11195 (2018).
- ¹⁹⁴S. Singh, B. Sharma, G. Banappanavar, A. Dey, S. Chakraborty, K. L. Narasimhan, P. Bhargava, and D. Kabra, *ACS Appl. Energy Mater.* **1**, 1870–1877 (2018).
- ¹⁹⁵Y.-Z. Zheng, X.-T. Li, E.-F. Zhao, X.-D. Lv, F.-L. Meng, C. Peng, X.-S. Lai, M. Huang, G. Cao, X. Tao, and J.-F. Chen, *J. Power Sources* **377**, 103–109 (2018).
- ¹⁹⁶Q. Guo, F. Yuan, B. Zhang, S. Zhou, J. Zhang, Y. Bai, L. Fan, T. Hayat, A. Alsaedi, and Z. Tan, *Nanoscale* **11**, 115–124 (2019).
- ¹⁹⁷X. Li, W. Zhang, W. Zhang, H.-Q. Wang, and J. Fang, *Nano Energy* **58**, 825–833 (2019).
- ¹⁹⁸H. Xiong, Y. Rui, Y. Li, Q. Zhang, and H. Wang, *J. Mater. Chem. C* **4**, 6848–6854 (2016).
- ¹⁹⁹F. Li and M. Liu, *J. Mater. Chem. A* **5**, 15447–15459 (2017).
- ²⁰⁰E. T. Vickers, T. A. Graham, A. H. Chowdhury, B. Bahrami, B. W. Dreskin, S. Lindley, S. B. Naghadeh, Q. Qiao, and J. Z. Zhang, *ACE Energy Lett.* **3**, 2931–2939 (2018).
- ²⁰¹G. Abdelmageed, H. R. Sully, S. Bonabi Naghadeh, A. El-Hag Ali, S. A. Carter, and J. Z. Zhang, *ACS Appl. Energy Mater.* **1**, 387–392 (2018).
- ²⁰²T. Mahmoudi, Y. Wang, and Y.-B. Hahn, *ACE Energy Lett.* **4**, 235–241 (2018).
- ²⁰³S. Bonabi Naghadeh, B. Luo, G. Abdelmageed, Y.-C. Pu, C. Zhang, and J. Z. Zhang, *J. Phys. Chem. C* **122**, 15799–15818 (2018).
- ²⁰⁴P.-T. Chen, T.-Y. Yung, T.-Y. Liu, C.-W. Sher, and M. Hayashi, *Chem. Phys. Lett.* **686**, 203–211 (2017).
- ²⁰⁵L. Zhang, F. Yu, L. Chen, and J. Li, *Appl. Surf. Sci.* **443**, 176–183 (2018).
- ²⁰⁶H.-H. Huang, Y.-C. Shih, L. Wang, and K.-F. Lin, “Boosting the ultra-stable unencapsulated perovskite solar cells by using montmorillonite/CH₃NH₃PbI₃ nanocomposite as photoactive layer,” *Energy Environ. Sci.* (published online).
- ²⁰⁷W. Li, C. Zhang, Y. Ma, C. Liu, J. Fan, Y. Mai, and R. E. I. Schropp, *Energy Environ. Sci.* **11**, 286–293 (2018).
- ²⁰⁸Y. Hou, Z. Ren Zhou, T. Yu Wen, H. Wei Qiao, Z. Qing Lin, B. Ge, and H. Gui Yang, *Nanoscale Horiz.* **4**, 208–213 (2019).
- ²⁰⁹T. M. Koh, V. Shanmugam, X. Guo, S. S. Lim, O. Filonik, E. M. Herzig, P. Müller-Buschbaum, V. Swamy, S. T. Chien, S. G. Mhaisalkar, and N. Mathews, *J. Mater. Chem. A* **6**, 2122–2128 (2018).
- ²¹⁰F. Zhang, D. H. Kim, and K. Zhu, *Curr. Opin. Electrochem.* **11**, 105–113 (2018).
- ²¹¹K. T. Cho, Y. Zhang, S. Orlandi, M. Cavazzini, I. Zimmermann, A. Lesch, N. Tabet, G. Pozzi, G. Grancini, and M. K. Nazeeruddin, *Nano Lett.* **18**, 5467–5474 (2018).
- ²¹²G. Grancini and M. K. Nazeeruddin, *Nat. Rev. Mater.* **4**, 4 (2019).
- ²¹³P. Chen, Y. Bai, S. Wang, M. Lyu, J.-H. Yun, and L. Wang, *Adv. Funct. Mater.* **28**, 1870113 (2018).
- ²¹⁴N. Li, Z. Zhu, C.-C. Chueh, H. Liu, B. Peng, A. Petrone, X. Li, L. Wang, and A. K.-Y. Jen, *Adv. Energy Mater.* **7**, 1601307 (2017).
- ²¹⁵X. Feng, R. Chen, Z.-A. Nan, X. Lv, R. Meng, J. Cao, and Y. Tang, *Adv. Sci.* **6**, 1802040 (2019).
- ²¹⁶W. Luo, C. Wu, D. Wang, Y. Zhang, Z. Zhang, X. Qi, N. Zhu, X. Guo, B. Qu, L. Xiao, and Z. Chen, *ACS Appl. Mater. Interfaces* **11**, 9149–9155 (2019).
- ²¹⁷J. Cao, C. Li, X. Lv, X. Feng, R. Meng, Y. Wu, and Y. Tang, *J. Am. Chem. Soc.* **140**, 11577–11580 (2018).
- ²¹⁸K.-T. Ho, S.-F. Leung, T.-Y. Li, P. Maity, B. Cheng, H.-C. Fu, O. F. Mohammed, and J.-H. He, *Adv. Mater.* **30**, 1870351 (2018).