Ab Initio Molecular Dynamics Simulations of Methylammonium Lead Iodide Perovskite Degradation by Water

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ABSTRACT: Protecting organohalide perovskite thin films from water and ambient humidity represents a paramount challenge for the commercial uptake of perovskite solar cells and, in general, of related optoelectronic devices. Therefore, understanding the perovskite/water interface is of crucial importance. As a step in this direction, here we present ab initio molecular dynamics simulations aimed at unraveling the atomistic details of the interaction between the methylammonium lead iodide (MAPbI₃) perovskite surfaces and a liquid water environment. According to our calculations, MAI-terminated surfaces undergo a rapid solvation process, driven by the interaction of water molecules with Pb atoms, which promotes the release of I atoms. PbI₂-terminated surfaces, instead, seem to be more robust to degradation, by virtue of the stronger (shorter) Pb–I bonds formed on these facets. We also observe the incorporation of a water molecule into the PbI₂-terminated slab, which could represent the first step in the formation of an intermediate hydrated phase. Interestingly, PbI₂ defects on the PbI₂-terminated surface promote the rapid dissolution of the exposed facet. Surface hydration, which is spontaneous for both MAI- and PbI₂-terminated slabs, does not modify the electronic landscape of the former, while the local band gap of the PbI₂-exposing model widens by ~0.3 eV in the interfacial region. Finally, we show that water incorporation into bulk MAPbI₃ produces almost no changes in the tetragonal structure of the perovskite crystal (~1% volume expansion) but slightly opens the band gap. We believe that this work, unraveling some of the atomistic details of the perovskite/water interface, may inspire new interfacial modifications and device architectures with increased stabilities, which could in turn assist the commercial uptake of perovskite solar cells and optoelectronic devices.

1. INTRODUCTION

Hybrid lead halide perovskites have rapidly emerged as promising new materials in the fields of photovoltaics and optoelectronics, thanks to their unique set of properties, such as small and tunable band gap,1 ambipolar charge transport properties,2,3 and limited charge recombination,4 which are regarded as a main loss channel.22,23 Leguy et al.24 have found that water vapor induces the reversible formation of MAPbI₃·H₂O and MAPbI₃·2H₂O hydrated species (MAPbI₃ = methylammonium lead iodide), which are reflected in an increased hysteresis in solar cell devices. Exposure of MAPbI₃ to liquid water produces irreversible perovskite decomposition to form PbI₂. Han et al.25 have reported that, at simulated environmental conditions (humidity up to 80%), the MAPbI₃ perovskite undergoes degradation after prolonged aging. Water-induced decomposition seemed to lead to the formation of HI, as originally proposed by Frost et al.,26 which was proposed to further react with the silver back-contact electrode layer.25 The perovskite degradation by water has also been discussed by Niu et al.,22 who reported that such reaction is thermodynamically

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favored in air. In a recent paper, Yang et al.\textsuperscript{23} reported a quantitative and systematic investigation of perovskite degradation processes, showing that the formation of a hydrated intermediate phase containing isolated PbI\textsubscript{6}\textsuperscript{4−} octahedra is the first step of the degradation mechanism. Similarly, Christians et al.\textsuperscript{27} have reported that an intermediate hydrated phase constitutes a key step in the water-induced degradation of MAPbI\textsubscript{3}. The degradation process seems to be assisted by photoexcitation, which supposedly weakens the hydrogen bonds between MA and the inorganic scaffold,\textsuperscript{28} and therefore favors the interaction between water molecules and the perovskite. In fact, computational modeling predicts a quite strong interaction between the MAPbI\textsubscript{3}, inorganic scaffold and water molecules, which will presumably modify the perovskite crystal structure.\textsuperscript{29}

In view of the detrimental effect of humidity on the integrity of hybrid perovskites, a great deal of research has been devoted to the development of adequate protecting strategies. To protect MAPbI\textsubscript{3} from degradation by moisture and suppress electron recombination between TiO\textsubscript{2} and spiro-MeOTAD, Niu et al.\textsuperscript{32} applied a device post-modification by adding an Al\textsubscript{2}O\textsubscript{3} layer acting as an insulator barrier, and a similar strategy was adopted by Dong et al.\textsuperscript{34} The hole-transport material may also play a crucial role in the protection of the perovskite from water-induced degradation,\textsuperscript{35,36} this material being deposited on the perovskite film side exposed to the counterelectrode. Accordingly, Habiserreitinger et al.\textsuperscript{30} applied a mitigation thermal degradation approach which increases the solar cell resistance to water ingress by replacing the organic hole-transport material with polymer-functionalized single-walled carbon nanotubes embedded in an insulating polymer matrix. It has also been shown that, in hole-transporting material-free perovskite devices, the presence of a 10 μm thick carbon layer back-contact acts as a water-retaining layer.\textsuperscript{31} Considering moisture as a main reason for perovskite degradation, vacuum production techniques have been devised to prevent water permeation in the perovskite.\textsuperscript{32} Surprisingly, however, in a recent paper, You et al.\textsuperscript{34} have described a perovskite growth process via thermal annealing of the precursor film in a humid environment (i.e., ambient air), which delivers greatly improved film quality, grain size, carrier mobility, and lifetime. This apparent contradiction prompts the commitment of further investigation in this direction. In this sense, experiments could greatly benefit from computer simulations, which should be able to provide the atomistic details of the perovskite/water interface and possible hints on the perovskite degradation process promoted by water.

In the work described in this paper, we carried out \textit{ab initio} molecular dynamics simulations to investigate the nature of the heterogeneous interface between water and the prototypical MAPbI\textsubscript{3} perovskite and to analyze the degradation and solvation processes which the perovskite may undergo in the presence of liquid water, along with a characterization of the solvated species. According to our calculations, MAI-terminated surfaces are easily prone to solvation, a process that is initiated by the nucleophilic substitution of dangling I ions on the surface by water molecules. Such a process is assisted by the concomitant solvation of neighboring MA cations. The PbI\textsubscript{2}-terminated surface, characterized by shorter Pb–I bonds compared to the bulk, is found to be less sensitive to the presence of interfacial water, suggesting that the PbI\textsubscript{2}-terminated surface could act as a protective layer. In the ~10 ps time scale amenable to our simulations, no degradation of the PbI\textsubscript{2}-exposing surface is observed; rather we find the infiltration of a water molecule into the intact perovskite cavity. Notably, (PbI\textsubscript{2})\textsubscript{n} “vacancy” defects, proposed by Haruyama et al.\textsuperscript{35} to easily form under PbI\textsubscript{2}-poor conditions, are found to substantially weaken the PbI\textsubscript{2}-terminated surface, leading to a cooperative degradation process which eventually produces solvated [PbI(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{5−} and [PbI\textsubscript{2}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{5−} species. We finally analyze the impact of hydration on the perovskite electronic structure, finding a general band gap increase upon perovskite interaction with water.

2. MODEL AND COMPUTATIONAL DETAILS

To simulate the perovskite surfaces, we have cut three 2×2 slabs from the bulk tetragonal MAPbI\textsubscript{3} crystal structure, which expose MAI- and PbI\textsubscript{2}-terminated and PbI\textsubscript{2}-defective surfaces, respectively; see Figure 1.

The exposed surfaces are the (001) ones, obtained from an optimized bulk structure showing an isotropic arrangement of the MA organic cations. By following the approach reported by Tateyama and co-workers,\textsuperscript{36} a stable defective surface was generated by removing six out of a total of eight of PbI\textsubscript{2} units from the PbI\textsubscript{2}-terminated surface. The employed periodic cell dimension are \(a = b = 17.71\ \text{Å}\), corresponding to twice the tetragonal experimental \(a = b\) cell parameters.\textsuperscript{37} For the simulation in water, we use \(\varepsilon = 49.67\ \text{Å}\) for all slabs, and we fill the vacuum region above and below the perovskite slab with water molecules, see Figure 1, employing the experimental density of liquid water. This approach includes at least the same water/perovskite volume in the PbI\textsubscript{2}-terminated simulation, with larger ratios for the MAI-terminated and for the PbI\textsubscript{2}-defective cases. The numbers of water molecules for the MAI-terminated, PbI\textsubscript{2}-terminated, and PbI\textsubscript{2}-defective surfaces are 284, 226, and 235, respectively. For comparison, we also performed MD simulations of the bare slabs, i.e., without any water molecules, using the same \(a = b\) cell dimensions but leaving 10 Å of vacuum along the non-periodic direction orthogonal to the perovskite surface. Car–Parrinello molecular dynamics\textsuperscript{36} (CPMD) simulations have been carried out with the Quantum Espresso package\textsuperscript{36} along with the GGA-PBE\textsuperscript{37} functional. For all calculations, electron–ion interactions were described by scalar relativistic ultrasoft pseudopotentials with electrons from O, N, and C 2s, 2p; H 1s; Ti 3s, 3p, 3d, 4s; I 5s, 5p; and Pb 6s, 6p, 5d shells explicitly included in the calculations. Plane-wave basis set cutoffs for the smooth part of the wave functions and the augmented density were 25 and 200 Ry, respectively. CPMD simulations have been performed with an integration time step of 10 au, for a total simulation time of ca. 10 ps. The fictitious mass used for the electronic degrees of freedom is 1000 au, and we set the atomic masses to an identical value of 5 amu to enhance the dynamical sampling. Initial randomization of the atomic positions has been used to reach a temperature of 350 ± 30 K.
without further applying any thermostat. Variable cell geometry optimization of the 4MAPbI3·H2O system was carried out using the PWscf code, with a 4×4×4 k-point mesh, plane-wave basis set cutoffs for the smooth part of the wave functions and the augmented density of 50 and 400 Ry, respectively and including dispersion contributions. The formation energy of the 4MAPbI3·H2O phase has been evaluated as follows: ΔH_total = E(4MAPbI3·H2O) − E(4MAPbI3) − E(H2O). Geometry optimization and density of states (DOS) analysis on the hydrated slabs have been carried out using the PWscf code, with plane-wave basis set cutoffs for the smooth part of the wave functions and the augmented density of 25 and 200 Ry, respectively.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization. To characterize the atomic structure of the bare MAI- and PbI2-terminated slabs, we have calculated their radial distribution functions (RDFs), averaged over the CPMD trajectories, and compared those of the bare slabs to that obtained for the bulk perovskite; see Supporting Information. The main features in the RDF of the bulk system are still recognizable in the bare MAI- and PbI2-terminated slabs, despite slightly broader, meaning that the finite size of our models does not significantly affect the crystal structure of the perovskite. This analysis also reveals that the equatorial Pb–I bond lengths of the bulk and the MAI-terminated slabs essentially coincide (average 3.21 Å), but they are slightly longer than those found for the PbI2-terminated slab (average 3.19 Å). From these numbers, it seems that the equatorial Pb–I bonds in the PbI2-terminated surface are stronger than in the bulk, suggesting that this facet may act as a protective layer on the perovskite; see below.

To characterize the interface between the perovskite facets and the surrounding liquid water environment, we have studied the possible interactions between water molecules and each of the exposed surfaces; see Figure 2. For the MAI-terminated surface, Figure 2a, water molecules could bind to either surface I anions (I–Hw bonds) or MA cations (HMA–O bonds). The calculated RDFs reveal I–Hw and HMA–O average distances of 2.57 and 1.75 Å, respectively, in the typical range of the respective hydrogen bonds. We also checked the Pb–O RDF, which reveals the formation of a small number of quite short Pb–O bonds (2.75 Å), suggesting that solvent molecules are able to percolate in the network formed by I and MA ions and reach the Pb atoms underneath. In fact, this is a crucial step for the release of the I anions; see below. Turning our attention to the PbI2-terminated facet, we report in Figure 2b the calculated Pb–O and I–Hw RDFs, which are related to the adsorption of water molecules on the perovskite surface. We found short bonds between the water oxygen atoms and the surface metal atoms, amounting to ~2.5 Å, suggestive of a rather strong interaction. Pb2+ is considered of borderline hardness acid in the Pearson’s hard and soft acids and bases theory, and as such it is able to form bonds with both soft ligands (such as the I–) in the MAPbI3 perovskite) and hard bases (such as H2O). Regarding the I–Hw interactions, we observed a broad distribution of such pairs, suggestive of a weaker (and less directional) interaction between the solvent molecules and the equatorial halogen atoms on the PbI2-terminated surface.

An interesting structural feature of MAPbI3 is the dynamics of MA cations, which is briefly discussed here, focusing on the φ angle, i.e., the angle formed between the perovskite ab plane and the CN axis of the organic cations. In the bulk phase, the MA cations have two preferred orientations, φ = ±30°, which were initially isotropically distributed in the bulk optimized structure originating the slabs. For the bare MAI-terminated slab, the MA cations in the outermost layers rotate to place their NH3 group close to the perovskite surface with the CH3 moiety pointing away from the slab; see Supporting Information. This is due to the stabilizing hydrogen bond between the ammonium group and the dangling I atoms at the MAPbI3 surface. In the innermost layer, instead, the MA cations seem to recover the original orientation, with two main peaks centered at ±30°. Upon hydration, the MA cations on the MAI-terminated facets lose their preferential orientation, since the surface MA cations are now able to form hydrogen bonds with the interfacial water molecules. For the PbI2-terminated slab, the picture is less well defined, with the MA cations showing a slight preferential orientation with the NH3 groups pointing to the surface, where they form hydrogen bonds with the surface I ions. This new pattern has little effect on the inner layers, where the MA molecules display the typical sharp features at ±30°. The hydrated system displays a broad distribution of φ angles, even in the innermost layers; see Supporting Information.

3.2. Perovskite/Water Interactions and Degradation Reactions. To investigate the dynamics of the perovskite/water interactions and the ensuing reactivity, we report in Figure 3a,b the time evolution of relevant geometrical parameters characterizing the dynamics of the MAI-terminated surface. Visual inspection of a series of geometrical configurations extracted from the CPMD simulations reveals that, following the attack of a water molecule to a surface I atom, Figure 3a, a seven-coordinated surface Pb center is formed, followed by the replacement of I by H2O in the Pb coordination sphere and the solvation of I exiting as an anion. This is clearly revealed by inspecting the time evolution of the Pb–O, Pb–I, and Pb–N distances, Figure 3b, illustrating
the key stages of the I release. In a first step, a water molecule approaches the perovskite surface and binds a Pb cation. As the Pb–H₂O bond is formed, the Pb–I bond weakens in a concerted fashion, since the Pb–I bond length increases as the Pb–H₂O distance decreases. Interestingly, the release of the I anion triggers the detachment of a neighboring MA cation from the perovskite surface, as shown by the increased distance between such a MA cation and its closest Pb atom. The solvated MA cation is supposed to stabilize the I anion in solution via hydrogen bonds. Moreover, this mechanism prevents positive charge accumulation on the MAPbI₃ facet, which could ultimately destabilize the crystal. Overall, in just 8.5 ps, we observe the solvation of one MAI unit. Although this time scale is definitely not representative of the experimental reaction kinetics, our data clearly suggest a very fast (and energetically favorable) process. This is in agreement with a very recent experimental work by Hailegnaw et al., in which MAI solvation has been identified as the first step of MAPbI₃ degradation.

Contrary to the MAI-terminated surface, in the time scale considered here, the PbI₂-terminated surface undergoes no decomposition reaction, despite the strong interaction of water molecules with surface Pb atoms; cf. Figure 2b. According to our results, the PbI₂-terminated surface is apparently more stable against water degradation than the MAI-terminated one, in keeping with the shortest (and thus stronger) Pb–I bonds characterizing the bare PbI₂-terminated slab. Most notably, for the PbI₂-terminated surface, we observe incorporation of one water molecule into the MAPbI₃ perovskite cavity. As one may notice from Figure 3c, at ~1 ps after thermalization, a water molecule crosses the PbI₂-terminated facet, as accounted for by the time evolution of the relevant geometrical parameters reported in the Supporting Information. An initially surface Pb-coordinated water molecule, bound to the outermost perovskite PbI₂ layer, reaches the cavity between the first and second PbI₂ layers, forming a hydrogen bond with one of the MA cations and remaining "trapped" in the cavity for the residual simulation time; see Supporting Information. Interestingly, the pathway of the water molecule across the interfacial PbI₂ layer deforms only slightly the inorganic scaffold, in such a way that the MAPbI₃ slab preserves its integrity. In Figure 3d, we monitor the trajectory of the water molecule in the perovskite ab plane along the dynamics. As it is immediately clear, the water molecule is preferentially located on the sides of the perovskite cavity, close to the inorganic scaffold, where it can form hydrogen bonds with the I atoms; see Figure 3d. In the time scale considered here, the water molecule samples two different sides of the perovskite cavity. The water molecule is further stabilized by the coupled motion of a MA cation, which forms hydrogen bonds with the water O atom. In fact, the MA cation rotates during the dynamics to follow the trajectory of the water molecule, with the ammonium group pointing toward the water molecule; see Figure 3d.

To investigate the possible role of surface defects in determining the stability of the water/perovskite interface, we further modeled a PbI₂-defective slab, which is likely to be stable under PbI₂-poor conditions. To this end, we took the PbI₂-terminated surface, which seems to be quite inert in its clean form, and we removed six PbI₂ units, leaving two undercoordinated Pb atoms on the exposed surface. This choice is inspired by previous theoretical works by Tateyama and co-workers, in which (PbI₂)ₙ vacancies were found to be stable...
under PbI₂-poor conditions. Inspection of the data in Figure 4 clearly reveals that this kind of defective facet undergoes fast
degradation processes. In particular, the two under-coordinated Pb atoms rapidly desorb from the perovskite surface, leading to the formation of solvated species; see Figure 4a,b. One of the Pb atoms is initially anchored to the perovskite surface through three I atoms, while one water molecule adds to the coordination sphere; see Figure 4a. The other surface Pb atom is initially bound to three I atoms on the perovskite surface and to two interfacial water molecules; see Figure 4b. During the CPMD trajectory, both surface Pb atoms depart from the perovskite surface and form octahedral [PbI₂(H₂O)₄]⁻ and [PbI(H₂O)₅]⁺ complexes in solution; see Figure 4a,b. The formation of both solvated complexes is shown in Figure 4c, where the coordination number of the two under-coordinated Pb atoms is monitored along the CPMD trajectory. From our simulations, it is clear that imperfections on the perovskite surface could further trigger the degradation of MAPbI₃. Therefore, the growth of defect-free crystals and thin films seems to be crucial to stabilize the perovskite material and preserve its integrity in the presence of humidity.

### 3.3. Impact of Water on the MAPbI₃ Electronic Structure

To check the impact of surface hydration on the electronic structure of the MAI- and PbI₂-terminated surfaces, we investigated the interaction between the considered slabs and a monolayer of eight water molecules, corresponding to saturation of all the surface under-coordinated sites; see Figure 5. It is worth noting that the formation energies of the hydrated slabs are $-0.49$ and $-0.44$ eV for the MAI- and PbI₂-terminated surfaces, respectively; thus, a considerable driving force is calculated for surface hydration. In Figure 5, we plot the local DOS of the investigated MAPbI₃ slabs. We point out that the employed arrangement of the MA cations imposes no net dipole across the considered slabs, which are almost perfectly symmetric, allowing us to solely gauge the impact of surface termination and hydration. We also notice that, as previously reported, the use of scalar relativistic DFT fortuitously reproduces the band gap of MAPbI₃$^{41,42}$ due to error cancellation between spin−orbit coupling, which reduces the gap, and to post-DFT correlation effects, which increase the gap by roughly the same amount.$^{43}$ The effect of spin−orbit coupling was further shown to be modulated by the local MAPbI₃ structure, in particular by the PbI₄ octahedra tilting,$^{44}$ which are, however, almost constant across the simulated slabs. We thus expect scalar relativistic DFT to produce qualitatively correct results for the electronic structure variation in the investigated bare and hydrated systems.

For the bare MAI-terminated facet, the band gap widens when moving from the inner (bulk-like) to the outermost layers, driven by the stabilization of the valence band edge of the outermost regions compared to that of the inner MAPbI₃ region; see Figure 5a. This is likely due to the partly unscreened interaction of the MA cations with the outermost I atoms, pushing their energy levels downward. The opposite trend is found for the PbI₂-exposing slab, with a band gap that closes at the outermost layers, due to the presence of under-coordinated Pb atoms on the surface. While in the MAI-terminated case no surface states appear to intrude in the perovskite gap, suggesting a limited effect of MAPbI₃ boundaries on carrier recombination for the PbI₂-terminated surface, the localization of the valence band edge at the perovskite surface may lead to trapping of photogenerated holes. Hydrating the surface with a water monolayer produces almost no changes in the MAI-terminated model, since the water/perovskite interaction takes place mainly through hydrogen bonding to the MA cations. On the other hand, in the PbI₂-terminated case, the valence band edge is stabilized in the interfacial region with the water monolayer compared to the opposite non-hydrated surface. The water-induced valence band down-shift, due to restoration of the surface Pb atoms’ coordination sphere, is not compensated by an associated conduction band shift, eventually leading to a local band gap increase by $\sim 0.3$ eV.

Inspired by the infiltration of one water molecule in the PbI₂-terminated surface observed during the CPMD simulation, we finally investigated the electronic effect of water incorporation into the bulk perovskite, considering a bare 48-atoms tetragonal unit cell and the same cell with a single added water molecule. For these two systems, we carried out full relaxation of the atomic positions and cell parameters, finding that incorporation of one water molecule into the perovskite cavity is thermodynamically favored by 0.45 eV, in turn suggesting that the hydrated phase should form spontaneously, as seen during the CPMD evolution. From our calculations, the MAPbI₃ band gap increases slightly from 1.45 eV in the bare MAPbI₃ to 1.50 eV in the material containing one interstitial water molecule. Notably, the volume of the unit cell increases.
only slightly (1.3%) upon incorporation of one water molecule, maintaining the same tetragonal cell shape ($c/a = 1.47$ vs $1.48$ for the hydrated and bare MAPbI$_3$). This data suggest the presence of a new intermediate hydrated phase, with a $4:1$ (or less) MAPbI$_3$:H$_2$O stoichiometry, which preserves the typical perovskite structural and electronic parameters, apart from a slight band gap opening, different from the $1:1$ and $1:2$ MAPbI$_3$:H$_2$O phases reported by Leguy et al.\textsuperscript{24} Our data thus clearly indicate that the MAPbI$_3$ electronic properties may be modulated by small amounts of water, such as by exposure to humidity, without affecting the material’s structural parameters.

4. CONCLUSIONS

Understanding the effect of ambient conditions and controlling the organohalide perovskite stability is a crucial issue for the commercial uptake of perovskite solar cells and, in general, of any optoelectronic device based on such class of materials. The interplay between the perovskite substrate and humidity has received much attention, since this is believed to be one of the main perovskite degradation channels.

Here, we have presented a comprehensive computational study on the MAPbI$_3$/H$_2$O hetero-interface, aimed at understanding the atomistic details that rule the interaction between the perovskite and a water environment. In particular, we have considered MAI- and PbI$_2$-terminated MAPbI$_3$ facets, which are most probably the exposed facets under MAI-rich and MAI-poor conditions. According to our calculations, the MAI-terminated slabs undergo rapid solvation, driven by the interaction of water molecules with Pb sites, which prompts the release of I atoms. We observe a nucleophilic substitution of I by H$_2$O, which is accompanied by the desorption of MA molecules, giving rise to a net dissolution of a MAI molecule, in line with the experimentally proposed picture showing MAI dissolution as a preliminary degradation stage. For the PbI$_2$-terminated facet, instead, no solvation process is observed in the considered time scale. The Pb—I bonds are particularly short (strong) in this kind of surface termination, suggesting that they could act as a protective layer against the degradation of the perovskite. For the PbI$_2$-terminated surface, however, we still observe the percolation of a water molecule in the perovskite slab, to form a new hydrated bulk phase in which the perovskite maintains its structural integrity. Our CMPD simulations also demonstrate that PbI$_2$ defects in the PbI$_2$-terminated facet may trigger the facile solvation of the exposed surface and initiate the degradation of the entire perovskite material.

According to our calculations, the hydration of both the MAI- and PbI$_2$-terminated surfaces is exoergic, with calculated formation energies of $-0.49$ and $-0.44$ eV, respectively. Hydration produces almost no changes in the electronic state landscape of the MAI-terminated model, since the adsorption is driven by hydrogen bonds to the MA cations. For the PbI$_2$-terminated slab, instead, the valence band edge is stabilized in the interfacial region with the water monolayer, which eventually leads to a local band gap increase by $\sim 0.3$ eV. Inspired by the infiltration process observed for the PbI$_2$-terminated slab model, we finally studied the effect of water incorporation on the electronic properties of bulk MAPbI$_3$. According to our calculations, for a $4:1$ MAPbI$_3$:H$_2$O stoichiometry, the perovskite band gap increases only slightly upon water incorporation, passing from $1.45$ eV in the bare MAPbI$_3$ to $1.50$ eV in the material containing one water molecule. Remarkably, the tetragonal crystal structure of MAPbI$_3$ remains almost unchanged, with only a $\sim 1\%$ volume

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**Figure 5.** Isodensity plot of the local density of states across the various perovskite layers found in the [001] direction, i.e., along the crystal $c$ axis, in the band gap region for (a) the bare and hydrated MAI-terminated and (b) the PbI$_2$-terminated perovskite slabs. Also reported are the global band gap values. The vertical dashed lines represent the valence and conduction bands for an isodensity value of 1 state/eV.
expansion, suggesting that water could be effectively hosted by the perovskite buffer without being possibly noticed by conventional characterization techniques. This work, unraveling the atomistic details of the perovskite/H$_2$O interface, may inspire new interfacial modifications and device architectures with increased stabilities, which could in turn assist the widespread uptake of perovskite solar cells and optoelectronic devices.

**ASSOCIATED CONTENT**

Supporting Information

Figure S1, Pb–I RDFs of the bulk MAPbI$_3$ and the MAI- and Pbl$_2$-terminated bare slabs; Figure S2, distribution of the angles formed between the MA C–N axis and the perovskite ab plane, for the bare and hydrated MAI- and Pbl$_2$-terminated perovskite slabs; and Figure S3, incorporation of a water molecule into the Pbl$_2$-terminated slab, showing snapshots of the key steps and the evolution of the distances between the water oxygen atom and the lead atom in the first and second slab layers and water molecules and the MA hydrogen. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b01991.

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Notes

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**REFERENCES**


SUPPORTING INFORMATION OF

Ab initio Molecular Dynamics of MAPbI$_3$ Perovskite

Degradation in Water

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Figure S1. Pb–I Radial Distribution Functions of the bulk MAPbI$_3$ (black) and the MAI- (red) and PbI$_2$- (blue) terminated bare slabs.
Figure S2. Distribution of the angles formed between the MA C-N axis and the perovskite $ab$ plane, for the bare (left) and hydrated (right) MAI- (top) and PbI$_2$-terminated (bottom) perovskite slabs.
Figure S3. Incorporation of a water molecule into the PbI$_2$-terminated slab, showing the snapshots of the key steps (top), and the evolution of the distances (bottom) between the water oxygen atom and the lead atom in the first (H$_2$O-L1, red line) and second (H$_2$O-L2, blue line) slab layer and water molecules and the MA hydrogen (H$_2$O-H, blue line).