Compositional effect on water adsorption on metal halide perovskites

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1. Introduction

Metal halide perovskites are excellent light absorbers used in perovskite solar cells for its excellent optoelectronic properties including tunable band gaps, low exciton binding energy, high carrier mobility, long diffusion length, etc. [1–5]. Power conversion efficiency of perovskite solar cells has increased from about 9–10\% since 2009 to over 25\% in 2019 [6–13]. Despite above-mentioned advantages of perovskite solar cells, their commercial application is restricted by their insufficient stability. These instability issues include light-induced instability, thermal instability and moisture-induced stability, etc. [14–19].

Moisture-induced degradation of the metal halide perovskites and perovskite solar cells are one of the most important stability issues [20–24]. Considerable efforts have been devoted to the understanding of the underlying mechanisms. It is generally believed that water adsorbs on the surface of perovskites and forms intermediate species, weakening the intrinsic structure of perovskites and facilitating the decomposition of perovskites to the binary compounds (namely PbI\textsubscript{2} and MAI) [25–32]. It is also proposed that water adsorption on the surfaces of the perovskites, as the first step, plays a key role in the degradation of the perovskites [33–36].

Some researches focused on the water adsorption on the mostly common studied MAPbI\textsubscript{3}. Koocher et al. [33] calculated the interaction of water with the surfaces of primary perovskites, AMX\textsubscript{3} (A\textsuperscript{+} = MA\textsuperscript{+}, FA\textsuperscript{+}, Cs\textsuperscript{+}; M\textsuperscript{2+} = Pb\textsuperscript{2+}, Sn\textsuperscript{2+}; X\textsuperscript{–} = I\textsuperscript{–}, Br\textsuperscript{–}), by using Density Functional Theory (DFT) calculations and comprehensive chemical bonding analysis. We reveal that the hydrophilic group NH\textsubscript{3}\textsuperscript{+} of MA\textsuperscript{+} cation may be the cause for instability issues. We find that the adsorption of water on FAPbI\textsubscript{3} and CsPbI\textsubscript{3} are much weaker than on MAPbI\textsubscript{3} due to the less polarity of FA\textsuperscript{+} and Cs\textsuperscript{+}. When exchanging M\textsuperscript{2+} cations, water adsorption on MASN\textsubscript{3} is also less energetically favorable than on MAPbI\textsubscript{3} because of the weaker ionic interaction of H\textsubscript{2}O-MASN\textsubscript{3}. When exchanging X\textsuperscript{–} anion, water adsorption on MAPbBr\textsubscript{3} is slightly weaker than on MAPbI\textsubscript{3} due to the slightly weaker covalent interaction of H\textsubscript{2}O-MAPbBr\textsubscript{3}. Our results present a comprehensive understanding of the compositional effect on the interactions of water with perovskites and provide rational design strategies to improve their stability against moisture via compositional engineering.
shows better stability towards moisture than MAPbI_3 and FAPbI_3 due to the less decomposition energy of CsPbI_3 than that of MAPbI_3 and FAPbI_3. Zhang et al. [30] found stronger water adsorption on MAPbI_3 than on MAPbBrI, and they detailed the effect of halide anion on the deprotonation process of MA\(^+\) cation. Jong et al. [45] investigated the water intercalation in MAPbX_3 and they presented a decreasing interaction strength when X\(^-\) change from I\(^-\) to Br\(^-\) and Cl\(^-\), which means the increasing water resistant ability. Nevertheless, the effect of A\(^+\) cation and M\(^2+\) cation was not considered in their work. Thus, researchers studied either the effect of A\(^+\) cation or M\(^2+\) or X\(^-\) anion on the interactions of water on metal halide perovskites. However, a comprehensive theoretical study on a complete comparison of all perovskites – including various and combined substitutions and different surface terminations is rarely seen. Moreover, a quantitative analysis of the composition-structure-property relation between water with a complete set of perovskite compositions is also missing.

In this work, we focus on the effect of the composition of perovskites on the water adsorption. By using DFT calculations and chemical bonding analysis, we show that the substitution of FA\(^+\) or Cs\(^+\) for MA\(^+\) and Sn\(^2+\) for Pb\(^2+\) and Br\(^-\) for I\(^-\) changes the interaction strength between water and perovskites, therefore, changing their water-resistant property. In the rest of this article, we first present the computational details and then show all structural models and name the possible adsorption sites of water on perovskites. Thereafter, we report the atomistic structures, the adsorption energies and the chemical bonding characteristics of water adsorption on MAPbI_3. We then compare the results of MAPbI_3 with other perovskites, where the A\(^+\) or M\(^2+\) or X\(^-\) are exchanged in AMX_3 (A\(^+\) = FA\(^+\), Cs\(^+\); M\(^2+\) = Pb\(^2+\), Sn\(^2+\); X\(^-\) = I\(^-\), Br\(^-\)) respectively. We finally discuss the effect of perovskite composition on the water adsorption and their underlying mechanisms and implications of our findings.

2. Computational methods and structural models

2.1. Computational methods

2.1.1. DFT Calculations

The DFT calculations were performed with PAW pseudopotential method as implemented in the Vienna Ab Initio Simulation Package (VASP) [46,47]. The Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) exchange correlation was utilized [48]. The cut-off energy of the plane-wave basis was set to be 500 eV. Tetragonal structures were used for MA\(^+\) and FA\(^+\) perovskites and orthorhombic structures were used for Cs\(^+\) perovskites for the structural optimization of the bulk. Then, the optimized bulk structures were used to cleave 1 \times 1 (001) surface slabs with four repeating unit cells (including 4 AX-layers, 4 MX_2-layers and one AX-/MX_2- terminated surface) in the z direction, including a vacuum of 15 Å. Top four layers and water molecule were allowed to relax until the residual force on each atom is smaller than 0.02 eV/Å. A 4 \times 4 \times 3 k-point mesh is used for bulk and surface calculations, respectively. The adsorption energies of water on the surface of perovskites were calculated as following:

\[
E_{\text{ads}} = E_{\text{water@surface}} - \left( E_{\text{surface}} + E_{\text{water}} \right)
\]

The positive value of \(E_{\text{ads}}\) means water adsorption on the surface of metal halide perovskites is energetically unfavorable, indicating the hydrophobicity of perovskites. While the negative value of \(E_{\text{ads}}\) represents water adsorption on the surface of perovskites is energetically favorable, indicating the hydrophilicity of perovskites.

2.1.2. Chemical bonding analysis

In addition to the energy calculations, we have also carried out an in-depth analysis of the chemical bonding for a thorough understanding of the energy variations at each adsorption site of each perovskite surface. The atomic population analysis method, Density Derived Electrostatic and Chemical (DDEC6) [49-51] was used. The bonds of main interests are those between water and the perovskite surfaces, as well as the bonds with the subsurface layer of the AMX_3 perovskites. The strength of the chemical bonding was analyzed by analyzing both the ionic and covalent contributions to a bond. The ionic component of the bond was evaluated from the investigation of the DDEC6 net atomic charges, which quantifies the electron transfer between atoms. The negative net charge indicates the atom is gaining electrons; positive net charge indicates the opposite. The covalent component can be identified from the investigation of the DDEC6 bond order. Quantifying the number of electrons dressed-exchanged between two atoms, the DDEC6 bond order is a functional of the electron and spin magnetization density distributions. Its formalism allows it to overcome limitations which are present in other bond order formulations. Thus, DDEC6 bond order approach exhibits good results when used in combination with various quantum chemistry methods (DFT- or wavefunction-based) and over a diverse set of materials and interactions [51]. Its values correlate well with the bond energies, within families of sufficiently similar materials [52,53]. The higher the bond order, the stronger the covalent bond. Similar approach has been used previously to investigate the interactions and reactivity of various systems, e.g. metal halide perovskite [54,55], 2D materials [56,57], porous media – zeolites, MOFs [58-60], hydrogen diffusion [61], etc.

Fig. 1. Schematic structures of several types of metal halide perovskite surfaces. MAPbI_3 (±/−) surface denotes that NH_3 or CH_3 pointing to the surface (highlighted by an upward/downward arrow). (a) and (c) are MAI-terminated MAPbI_3 surfaces. (b) and (d) are PbI_2-terminated MAPbI_3 surfaces. (e) FAI-terminated and (f) PbI_2-terminated FAPbI_3 surface. (g) CsI-terminated and (h) PbI_2-terminated CsPbI_3 surface.
3. Results and discussions

Fig. 2, respectively.

The oxygen atom of the water (O) tends to interact with one of the hydrogen atoms of NH$_3$ (H$_3$) compared to the hydrogen of CH$_3$ (H$_3$). Here, the water interacts with the surface via two bonds including O with H$_3$ (O-H hydrogen bond) and hydrogen of water (H$_2$O) with iodine atom (H-I hydrogen bond). The interaction of water with a $\omega^-$ site is strong (adsorption energy of $-0.48$ eV), evidenced by the small distances of O-H$_3$ and H$_2$O-I being 1.80 Å and 2.54 Å, shown in Fig. 3c, respectively. While on a $\omega^-$ site, O does not tend to interact with H$_3$. Instead, H$_2$O rotates to form only a single H$_2$O-I bond (H$_2$O is 2.82 Å above I atom in Fig. 3d), which is also longer, and therefore weaker (adsorption energy of $-0.16$ eV) than the one at the (+) site. For the other sites on MAI-termination (i.e. $\beta^-$ and $\gamma^-$ sites), bond lengths of O-H$_3$ are evidently shorter (about 0.7 Å) than O-H$_3$ at $\beta^-$ and $\gamma^-$ sites, supporting overall weaker water adsorption at (-) sites than at (+) sites on MAI-terminated surface.

A detailed chemical bonding analysis of H$_2$O-MAPbI$_3$ allows us to get a deeper understanding of the underlying reasons for the observed trends in energies and structures. We see the consistent agreement between the stronger bond order of H$_2$O-MAPbI$_3$ and the more negative adsorption energy of water on MAPbI$_3$ (Fig. 3a, b). The only exception is the $\delta^-$ sites and the underlying reason is discussed in supporting information and shown in Fig. S1. In agreement with the energies and structures, on MAI-terminated surface, a stronger bond (larger bond order) between O and H$_3$ at (+) sites is found than that between O and H$_3$ at (-) sites. The different bond strength of the two O–H bonds is a consequence of a competition within the bonding of O–H–N (C), where the O is part of H$_2$O and H is part of NH$_3$ or CH$_3$ groups. The C–H$_3$ is stronger (bond order is 0.87) than N–H$_3$ (bond order is 0.74) (see also Table S2). The weaker N–H$_3$ bond leads to stronger O–H$_3$ bond (bond order: 0.21 at $\omega^+$ site) than O–H$_3$ (0.00 at $\omega^-$ site). In addition, N–H$_3$ bond is more polar than the C–H$_3$ and therefore more prone to be involved in hydrogen bonding [63]. As a result, NH$_3$ group is hydrophilic; while CH$_3$ is hydrophobic. Similar preference is found for the interaction of water with other absorption sites, where water maximizes its interaction with H$_3$ (bond order of O–H$_3$ around 0.12 at $\beta^-$ and $\gamma^-$) and minimizes it with H$_3$ (bond order of O–H$_3$ around 0.05 at $\beta^-$ and $\gamma^-$), explaining the fact the adsorption energies on the (+) sites are overall more negative (above 0.20 eV) than those on the (-) sites.

In contrast with the drastic changes in both energies and structures on the MAI-termination, the changes on the PbI$_2$-termination are relatively small. This is because the effect of MA$^+$ cation (now located in the sub-surface) is less dominating now. Indeed, the main difference is coming from the interaction strength of MA$^+$ with the inorganic framework on the surface: a slightly stronger hydrogen bond of I–NH$_3$ (total bond order of 0.14) than I–CH$_3$ (total bond order of 0.04) leads to slightly weaker adsorption of H$_2$O on (+) sites than on (-) sites (Table S3). Therefore, water slightly favors (-) sites than (+) sites. However, we note that here all adsorption energies found on the PbI$_2$-termination are quite large due to the very strong O–Pb bonds (bond order: ~0.30, Fig. S2) and moderately strong H$_2$O-I interaction (bond order: around 0.17 at (+) sites and 0.26 at (-) sites, Fig. S2).

All the above analysis indicates that the adsorption of water on all MAPbI$_3$ surfaces are overall strong, with the only exception when it is in direct contact with the hydrophobic CH$_3$ group of MA$^+$ cation. This agrees with the previous reports on the strong interaction of water on the MAPbI$_3$, in particular with the NH$_3$ group [26]. This strong

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**Table 1**

| Columns     | AX-terminated surface | MX2-terminated surface | Adsorption sites |
|-------------|------------------------|-------------------------|-----------------|
| MAI-terminated surface | α⁺ | NH$_3$ group pointing to the surface | above halide ion |
|             | α⁻ | CH$_3$ group pointing to the surface | above halide ion |
|             | β⁺ | NH$_3$/NH$_2$ group pointing to the surface | above one hydrogen of NH$_3$/NH$_2$ group |
|             | β⁻ | CH$_3$/CH$_2$ group pointing to the surface | above one hydrogen of CH$_3$/CH$_2$ group |
|             | γ⁺ | NH$_3$ group pointing to the surface | above one hydrogen of CH$_3$ group |
|             | γ⁻ | CH$_3$/CH$_2$ group pointing to the surface | above one hydrogen of NH$_3$/NH$_2$ group |
| MX2-terminated surface | ε⁺ | NH$_3$ group pointing to the surface | above M–X bond |
|             | ε⁻ | CH$_3$ group pointing to the surface | above M–X bond |
|             | δ⁺ | NH$_3$/NH$_2$ group pointing to the surface | above the four-fold halide site |
|             | δ⁻ | CH$_3$/CH$_2$ group pointing to the surface | above the four-fold halide site |
|             | ζ⁺ | NH$_3$ group pointing to the surface | above metal ion |
|             | ζ⁻ | CH$_3$ group pointing to the surface | above metal ion |
3.2. The effect of A⁺ cation

To evaluate the effect of A⁺ cation, we investigated the adsorption of H₂O on FAPbI₃ and CsPbI₃ surfaces and further compared them with those on MAPbI₃ surfaces. We find that the adsorption energies on FAPbI₃ and CsPbI₃ surfaces are generally less negative than those on MAPbI₃ (Fig. 4a), which indicates that water is less favorable to adsorb on FAPbI₃ and CsPbI₃. We rationalize the findings below by comparing the structures and analyzing the chemical bonding, while the exception of water bonding at β⁻ and δ sites is discussed in the supporting information.

On Al-termination, as shown above with the case of MA⁺, the
difference in the optimized position of water between $\alpha^+$ site and $\alpha^-$ site depend very much on the hygroscopicity (polarity) of $A^+$ cation: water prefers to adsorb at the sites where the hydrophilic NH$_3$ group points to the surface rather than the hydrophobic CH$_3$ group. Interestingly, the optimized position of water as well as their adsorption energies at $\alpha^+$ site of FAPbI$_3$ and CsPbI$_3$ are similar to $\alpha^-$ site of MAPbI$_3$, when the hydrophobic CH$_3$ group points to the surface. As presented in Fig. 4c–e, the bond distances of HW-I on FAPbI$_3$ and CsPbI$_3$ are all similar with that on MAPbI$_3$ (within ± 0.15 Å) at $\alpha^+$ site. The O–A$^+$ bond length of CsPbI$_3$ (3.10 Å, Table S4) are longer than that of MAPbI$_3$ (1.88 Å) while comparable between MAPbI$_3$ and FAPbI$_3$ (1.80) at $\beta^+$ site. This indicates that the surfaces of FAPbI$_3$ and CsPbI$_3$ are likely to repel water and are similar to the surface of MAPbI$_3$ when the hydrophobic CH$_3$ group points to the surface.

As shown earlier, the evaluation of bond order between H$_2$O and MAPbI$_3$ is a useful tool to understand and quantify the effect of various adsorption sites on the absorption energies of H$_2$O. However, it’s not straightforward to compare the chemical bond strength from bond orders with various covalent/ionic ratios are present. This is possibly the reason we observe certain discrepancies when we vary the $A^+$ cation and we look at the bond orders of the bonds between H$_2$O and the surfaces of APbI$_3$ (Fig. 4a, b). Very different characters of $A^+$ cation (organic, inorganic) lead to bonds which are significantly different and not easily comparable [52,53]. In Fig. 4f we observe that the FA$^+$ bonds including N–H (bond order of 0.95 to 0.99) and C–H (bond order of 0.99) are with similar strength, and much stronger than the N–H (0.74) and slightly stronger than C–H (0.87) bonds from MA$^+$. As a consequence FA$^+$ will be less reactive than MA$^+$Furthermore, MA$^+$ is more polar than FA$^+$ and Cs$^+$ [64], evidenced by the less symmetric bond orders in Fig. 4f and charge distribution from net atomic charges of all atoms in Fig. S2aH$_2$O as a polar molecule tends to interact with polar cations. Less polarity in FA$^+$ and Cs$^+$ lead to energetically unfavorable absorption of water on FAPbI$_3$/CsPbI$_3$ than MAPbI$_3$. Therefore, our analysis suggests that substituting or mixing polar molecule MA$^+$ cation with less polar cations, such as FA$^+$, Cs$^+$ and GA$^+$ (C(NH$_2$)$_3$$^+$) can be a feasible strategy for improving the water resistance of metal halide perovskites[38].

On PbI$_2$-termination, the adsorption energies of water on FAPbI$_3$ and CsPbI$_3$ do not change as significantly (energy differences within 0.04 eV) when comparing with MAPbI$_3$, as it was the case for the AX-terminated surfaces, with majority of interactions being slightly weaker (bond length of O–Pb with differences within 0.05 Å). And the adsorption energies of FAPbI$_3$ and CsPbI$_3$ are closed to the more hydrophobic (+) surfaces of MAPbI$_3$, except for the $\delta$ sites. This is because of the stronger interaction of the subsurface cations with the surface I atoms leads to overall slightly weaker H$_2$O-I interactions. In particular, FA$^+$-I bonds with a total bond order of 0.39 (in Table S5) and Cs$^+$-I bonds with a total bond order of 0.18 are both larger than that of the (+) surface of MA$^+$-I (0.17).

### 3.3. The effect of M$^{2+}$ metal

M$^{2+}$ divalent cation also affects water adsorption on perovskites. The calculated adsorption energies of water on MASnI$_3$ are generally

### Table 2

Comparison of adsorption energies of water on MAPbI$_3$ of this work and previous studies [33].

| Adsorption sites | $E_{\text{ads}}$ on (+) surface/eV | $E_{\text{ads}}$ on (−) surface/eV |
|-----------------|----------------------------------|----------------------------------|
| MAI-terminated surface | | |
| $\alpha$ | −0.48 | −0.49 |
| $\beta$ | −0.34 | −0.36 |
| $\gamma$ | −0.45 | −0.48 |
| PbI$_2$-terminated surface | | |
| $\epsilon$ | −0.45 | −0.40 |
| $\delta$ | −0.31 | −0.38 |
| $\zeta$ | −0.45 | −0.39 |

### Fig. 3.

Comparison of water adsorption on several surface sites on MAPbI$_3$. (a) Adsorption energies ($E_{\text{ads}}$), (b) bond orders, (c) optimized structure of H$_2$O-MAPbI$_3$ (with the display of bond lengths as black numbers and bond orders as blue) on $\alpha^+$ site of MAPbI$_3$ and (d) at $\alpha^-$ sites of MAPbI$_3$. The energies and bond orders of the structures (c) and (d) are highlighted by circles in panels (a) and (b).

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1. As mentioned earlier the exception from the $\delta$ sites is discussed in the supporting information.
less negative than those on MAPbI3. We observe the same trend in adsorption energies influenced by the orientation of MA+ cations, i.e., on MAI-termination, $E_{\text{ads}}$ at (−) sites being less negative than that at (+) sites; on MI2-termination, $E_{\text{ads}}$ at (+) sites are less negative than that at (−) sites.

The adsorption energies on MAI-terminated surface do not show an obvious change for each adsorption site when Pb2+ is exchanged with Sn2+ (Fig. 5a), with differences in energy within less than 0.05 eV. On the MI2-termination, the adsorption energies of water on the SnI2-terminated surfaces are in general (about 0.1 to about 0.3 eV) less negative than those on PbI2-terminated surface. We note here that the structural details including bond lengths and bond orders of H2O-MAPbI3 and H2O-MASnI3 do not provide direct evidences for the energy differences (Table S6). For example, at $\epsilon$− site from Fig. 5c, d, we find slightly shorter M–O bond (0.09 Å shorter) as well as slightly longer H–I (0.06 Å and 0.09 Å longer) bonds on MASnI3 than those on MAPbI3. This can be further understood by considering both the covalent and ionic interactions of water molecules with the surfaces of MAI3 as following.

On MI2-terminated surface, the O with the lone pair electron interacts with the metal divalent acceptor, while H2O accepts interact with iodine which act as the donors. On the one hand, we found very similar covalent interaction of H2O-MASnI3 and H2O-MAPbI3 from bond orders in Fig. S3a; on the other hand, we observe significant differences in net atomic charges in Fig. 5b, which depends significantly on the electronegativity of M2+ cation. With an electronegativity of Pb (2.3) being closer to that of I (I: 2.5, Sn: 1.8) [65–67], the net atomic charge of Pb (~0.84) is more positive than Sn (~0.70) as depicted in Fig. 5b. As a result, the attraction of Pb with O is stronger than that of Sn, i.e. stronger ionic interaction of O–Pb ($1.92 \times 10^9$ N) than O–Sn ($1.64 \times 10^9$ N) according to Coulomb’s law (Eq. (1)). Furthermore, the net atomic charge of I (~0.70) in MAPbI3 is more negative than I (~0.44) in MASnI3. Consequently, it leads to a stronger interaction between H2O-I on MAPbI3 than on MASnI3. Taking into account the

![Fig. 4. Comparison of water adsorption on APbI3 perovskites (A = MA+, FA+ and Cs+). (a) $E_{\text{ads}}$, (b) bond orders, (c) optimized position (bond length in black) and bond orders (in blue) for H2O-MAPbI3 on $\alpha^-$ sites of MAPbI3, (d) on $\alpha^+$ sites of FAPbI3, (e) on $\alpha^+$ sites of CsPbI3, (f) bond orders within MA+ and FA+ cations. The energies and bond orders of the structures (c), (d) and (e) are highlighted by circles in (a) and (b).](image-url)
similar covalent interactions (analyzed above) and the weaker ionic interaction of H$_2$O-MASnI$_3$ compared to H$_2$O-MAPbI$_3$, we explain the less favorable adsorption of water on MASnI$_3$ than on MAPbI$_3$ through the ionic contributions.

$$F = K_e \frac{q q'}{r^2}$$

(1)

$q = 1.60 \times 10^{-19} \times \text{net atomic charge}$

where $K_e$ is Coulomb's constant ($K_e \approx 9 \times 10^9 \text{N} \cdot \text{m}^2 \cdot \text{C}^{-2}$), $q$ and $q'$ are the charges of the two atoms, and the $r$ is the distance between these two atoms.

### 3.4. The effect of $X^-$ halide

Water adsorption on perovskites is slightly influenced by the $X$ halide. Overall, from Fig. 6a, the change in $E_{ads}$ between MAPbI$_3$ and MAPbBr$_3$ is small, with the values on MAPbBr$_3$ being slightly less negative than those on MAPbI$_3$. For instance, at the $\gamma^-$ sites, water adsorption energy on MAPbBr$_3$ is slightly less negative by $\sim 0.04$ eV than those on MAPbI$_3$ (see Fig. 6a). Moreover, the same trend as in Section 3.2 in adsorption energies is found on MAX-termination, $E_{ads}$ at ($\gamma^-$) sites are less negative than that at ($\gamma^+$) sites; on PbX$_2$-termination, the trend in $E_{ads}$ is reversed. This shows that the orientation of MA$^+$ dominates the changes in the adsorption energies on both MAX-terminated and PbX$_2$-terminated surfaces regardless of the types of metal cation or halide anion.

The bond length of H$_2$O-MAPbX$_3$ (Table S7) also demonstrates that water has slightly less affinity with surfaces of MAPbBr$_3$ than those of MAPbI$_3$. This is attributed to the slightly weaker covalent interaction of H$_2$O-Br than H$_2$O-I (shown in Fig. 6b and Fig. S4a). This is demonstrated also by the example shown in Fig. 6c, d, where water interacts with two I atoms (with bond orders of 0.11 and 0.06) on MAPbI$_3$ surface, but only with one Br atom on MAPbBr$_3$ (bond order of 0.14), as the second bond H$_2$O-Br$_2$ (3.96 Å) is too long and does not lead to an interaction (bond order: 0). Adding all contributions altogether, the interaction strength of H$_2$O-MAPbBr$_3$ is slightly weaker than that of H$_2$O-MAPbI$_3$. The exception case of $\alpha^-$ site is discussed in the supporting information.

On PbX$_2$-termination, similar trends are observed, slightly less negative $E_{ads}$ (within 0.05 eV) of water on MAPbBr$_3$ than on MAPbI$_3$. This is proven by the slightly weaker interaction of H$_2$O-MAPbBr$_3$ than H$_2$O-MAPbI$_3$ (difference of bond order within 0.03, the differences of bond length of O-Pb less than 0.04 Å and HW-X less than 0.3 Å). This indicates that water generally interacts less strongly with MAPbBr$_3$ not only for the MAX-termination but also for the PbX$_2$-termination. The above finding demonstrates that the substitution of I by Br is beneficial to repel water and to avoid the degradation induced by moisture.

### 3.5. Discussion

Our new results are further discussed and analyzed here in the context of the existing experimental results. In this work, we focus on the impact of the compositional change in the adsorption strength of water on diverse halide perovskite surfaces. We note that directly comparing our results with experiments is not straightforward because understanding the overall stability of perovskites is a complex scientific problem. In addition to the stability towards moisture, tuning the composition of the perovskite also impact the structural/phase stability [22], the morphology [54], the types and the concentration of intrinsic

![Figure 5. Comparison of water adsorption on MASnI$_3$ and MAPbI$_3$. (a) $E_{ads}$, (b) net atomic charge on M$I_2$-termination, (c) optimized positions (bond lengths in black) and net atomic charges (in dark green) for M-H$_2$O on $\varepsilon^-$ sites of MAPbI$_3$ and (d) MASnI$_3$. The energies and net atomic charges of structures (c) and (d) are highlighted by circles in (a) and (b).](image-url)
defects \cite{68} and more. Moreover, the moisture induced degradation of
perovskites is a collective/multistep process, involving adsorption on
the surfaces/grain boundary, infiltration and diffusion into the bulk,
and dissociation reactions \cite{35,36,69}.

Nevertheless, our analysis of the water adsorption strength on dif-
ferent perovskites is consistent with the existing experimental findings
that partially substituting MA\textsuperscript{+} with FA\textsuperscript{+} and Cs\textsuperscript{+} \cite{38,39} or partially
substituting I\textsuperscript{−} with Br\textsuperscript{−} \cite{1} enhanced the stability of MAPbI\textsubscript{3} towards
moisture. This indicates that the initial chemical bonding interaction of
water with the surface has important implications on overall degrada-
tion processes.

To obtain a more comprehensive understanding of the degradation
processes, molecular dynamics \cite{36,70,71} is a very useful method to
investigate kinetics and to study temperature effect. For example, ro-
tation of methylammonium was discovered in both experiments \cite{72}
and theoretical simulations \cite{73,74}. The rotation of MA\textsuperscript{+} was found to
be possible at room temperature and become more pronounced with
increasing temperature \cite{75}. Consequently, a dynamical interaction of
water with MA\textsuperscript{+} cations can be expected at high temperature. Par-
ticularly, the metal halide perovskites with a polar A\textsuperscript{+} cation (such as
MA\textsuperscript{+} and FA\textsuperscript{+} \textit{et al}. ) would be notably affected by the change of
temperature. Another important aspect that is not covered in this work
is the effect of water vapor (instead of one isolated water molecule).
Water vapor was previously proposed to play an important role in
solvating MA\textsuperscript{+} and I\textsuperscript{−} ions and inducing degradation reactions \cite{35}.

However, all above-mentioned dynamical properties are beyond the
scope of this study due to the high cost of \textit{ab-initio} methods. To fully
understand the collective mechanism of the water induced degradation
of perovskites, our future plan is to expand the current DFT study to
classical molecular dynamics simulations using reactive force fields
\cite{76–78}.

4. Conclusions

In summary, using DFT calculations and chemical bonding analysis,
we have investigated water adsorption on several primary metal halide
perovskites. We studied the adsorption energies, adsorption structures
and chemical bonding between water and MAPbI\textsubscript{3} and elucidated the
compositional effect of the perovskites by substituting FA\textsuperscript{+} and Cs\textsuperscript{+} for
MA\textsuperscript{+}, Sn\textsuperscript{2+} for Pb\textsuperscript{2+} and Br\textsuperscript{−} for I\textsuperscript{−} on their interactions with water.
We find that the adsorption of water on MAPbI\textsubscript{3} is overall strong with
the exception of surface sites near the hydrophobic CH\textsubscript{3} group of MA\textsuperscript{+}
cation. This points to the general knowledge of the instability of
MAPbI\textsubscript{3} towards moisture. When substituting FA\textsuperscript{+} or Cs\textsuperscript{+} for MA\textsuperscript{+},
adsorption of water on the surface of FAPbI\textsubscript{3} and CsPbI\textsubscript{3} is less favor-
able than on MAPbI\textsubscript{3}. This is mainly due to the smaller or zero polarity
(which means the more hydrophobic nature) of FA\textsuperscript{+} or Cs\textsuperscript{+} (which
leads to more hydrophobic surfaces). Our results indicate that sub-
stituting or partially substituting the polar MA\textsuperscript{+} with less polar FA\textsuperscript{+} or
nonpolar Cs\textsuperscript{+} can potentially increase the stability of the resulted
perovskites. When exchanging M\textsuperscript{2+} cations (Sn\textsuperscript{2+} for Pb\textsuperscript{2+}), due to the
weaker ionic interaction of H\textsubscript{2}O-MASnI\textsubscript{3} than H\textsubscript{2}O-MAPbI\textsubscript{3}, MASnI\textsubscript{3}
shows slightly better water resistance than MAPbI\textsubscript{3}. For different X\textsuperscript{−}
anion, the adsorption energy of water on MAPbI\textsubscript{3} and MAPbBr\textsubscript{3} are
comparable. Surprising result is that the interaction of water with
bromides is weaker than iodines though the ionicity of MAPbBr\textsubscript{3} is
higher than MAPbI\textsubscript{3}. The substitution of Br\textsuperscript{−} for I\textsuperscript{−} slightly weakens the
covalent interaction of H\textsubscript{2}O-MAPbX\textsubscript{3}, decreasing the possibility of

![Fig. 6. Comparison of water adsorption on MAPbI\textsubscript{3} and MAPbBr\textsubscript{3}. (a) \(E_{ads}\), (b) bond orders, (c) optimized positions (bond lengths in black) and bond orders (in blue)
of X-H\textsubscript{2}O on \(\gamma\) sites of MAPbI\textsubscript{3} and (d) MAPbBr\textsubscript{3}. The energies and bond orders of the structures (c) and (d) are highlighted by circles in (a) and (b).](image-url)
adhesion of water on MAPbBr\textsubscript{3}. The stronger interaction of I with water has to do with a stronger covalent bonding and a better geometrical compatibility of the water molecule with the I atoms at the surfaces (e.g. two H-I bonds compared to the single H-Br bond). Our study provides a comprehensive understanding of the effect of the perovskite composition on ad sorption on metallic halide perovskites and further provides the rational strategies to improve the stability against moisture through compositional engineering.

CRediT authorship contribution statement

Qihua Li: Investigation, Writing - original draft, Writing - review & editing, Formal analysis. Zehua Chen: Methodology, Writing - review & editing. Ionut Tranca: Methodology, Writing - review & editing. Silvia Gaasta-Nedea: Conceptualization, Writing - review & editing, Formal analysis, Supervision. David Smeulders: Supervision. Shuxia Tao: Conceptualization, Methodology, Writing - review & editing, Supervision, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Detail information on the bond lengths between water and AM\textsubscript{X}\textsubscript{3}; General information on the chemical bonding between water and composition of AM\textsubscript{X}\textsubscript{3}, bond orders between A + cation and surface atoms and internal bond orders within the MA\textsuperscript{+} cation; Explanations of the exception cases (δ sites, β site of FAPbI\textsubscript{3} and α site of MAPbX\textsubscript{3}).

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