Decomposition of Organic Perovskite Precursors on MoO$_3$: Role of Halogen and Surface Defects

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ABSTRACT: Despite the rapid progress in perovskite solar cells, their commercialization is still hindered by issues regarding long-term stability, which can be strongly affected by metal oxide-based charge extraction layers next to the perovskite material. With MoO$_3$ being one of the most successful hole transport layers in organic photovoltaics, the disastrous results of its combination with perovskite films came as a surprise but was soon attributed to severe chemical instability at the MoO$_3$/perovskite interface. To discover the atomic origin of this instability, we combine density functional theory (DFT) calculations and X-ray photoelectron spectroscopy (XPS) measurements to investigate the interaction of MoO$_3$ with the perovskite precursors MAI, MABr, FAI, and FABr. From DFT calculations we suggest a scenario that is based upon oxygen vacancies playing a key role in interface degradation reactions. Not only do these vacancies promote decomposition reactions of perovskite precursors, but they also constitute the reaction centers for redox reactions leading to oxidation of the halides and reduction of Mo. Specifically iodides are proposed to be reactive, while bromides do not significantly affect the oxide. XPS measurements reveal a severe reduction of Mo and a loss of the halide species when the oxide is interfaced with I-containing precursors, which is consistent with the proposed scenario. In line with the latter, experimentally observed effects are much less pronounced in case of Br-containing precursors. We further find that the reactivity of the MoO$_3$ substrate can be moderated by reducing the number of oxygen vacancies through a UV/ozone treatment, though it cannot be fully eliminated.

KEYWORDS: perovskite, metal oxide, DFT, photoelectron spectroscopy, stability

1. INTRODUCTION

Recently, metal halide perovskites have drawn unprecedented attention, due to their highly attractive properties, such as tunable band gaps and high carrier mobility that make them ideal for a range of optoelectronic applications. Within just a few years, perovskite solar cells (PSCs) have achieved efficiencies of >25%, a progress that took decades for other photovoltaic technologies. In early studies, the material of choice was MAPbI$_3$, while in the last years, more complex mixed perovskite compositions have been the focus of the research community. Nevertheless, there are issues that remain to be addressed for the commercialization of PSCs, especially when devices are exposed to humidity, light, elevated temperatures, or oxygen.

In addition to the active perovskite material, PSCs typically contain charge extraction layers, that selectively transport charges to the contacts. At such an interface, it is obviously important to ensure an appropriate alignment of energy levels to minimize losses in device performance. Good charge extraction can be achieved by a variety of organic molecules and polymers, metal oxides, or 2D materials.

Over the years, it has become clear that not only the energetic alignment plays a crucial role, but the chemical compatibility also has to be considered. While the contact between perovskites and organic charge extraction layers seems to be benign, strong redox or Lewis acid base reactions with metal oxides have been reported. Since metal oxides are essential in the development of low cost and large area devices, it is of paramount importance to understand the origin of these interface reactions between metal oxides and perovskites.

One notable example of detrimental interface decomposition concerns the material MoO$_3$. While in the field of organic photovoltaics MoO$_3$ is one of the most successful hole extraction layers, this success could not be replicated in PSCs, as devices with a MAPbI$_3$ absorber in contact with..
MoO$_3$ yield very low power conversion efficiencies. While the strong p-doping ability of MoO$_3$ is advantageous to facilitate hole extraction from an organic semiconductor layer, this capability to oxidize seems to be detrimental for perovskites. Several X-ray photoelectron spectroscopy (XPS) studies have attempted to elucidate the interaction between MAPbI$_3$ and this metal oxide by probing the elemental composition at the interface and found a decomposition of MA or FA molecules, a loss of iodide, and even a loss of lead. This is accompanied by changes in the element oxidation states, most prominently the severe reduction of Mo. While the previous studies all agree on the deterioration of, both, the MoO$_3$ and the perovskite, the underlying reaction mechanisms and reaction routes remain unclear.

Understanding the atomistic origin of the chemical instability could provide valuable insights regarding strategies to prevent or mitigate such issues at the perovskite–metal oxide interface. MoO$_3$ is of particular interest to study this interaction as it is known to be an extreme case, so interactions can be studied in detail. Here, to understand the mechanisms for degradation, it is important to analyze which component of the perovskite and which property of the metal oxide surface triggers the reactions. So far, XPS or Raman studies regarding perovskite degradation in contact to MoO$_3$ were mostly done using MAPbI$_3$. Therefore, it is not clear whether the instability is inherent to MoO$_3$, or if possibly the organic cation or the halide species are responsible. Such investigations can best be done using only the organic cation precursors, as for example shown in studies on other metal oxides such as NiO and TiO$_2$. These publications showed that precursor materials undergo similar decomposition reactions compared to the perovskite material.

In this work, we combine density functional theory (DFT) calculations with experimental XPS investigations to shed light on the interaction between MoO$_3$ and various organic perovskite precursors AX (A = MA, FA; X = I, Br). From DFT calculations on model MoO$_3$ surfaces and precursor molecules we try to identify probable reaction pathways that can degrade the AX precursors and reduce the metal oxide. This allows us to disentangle the influences of organic cations from those of the halide species on this surface. These calculations point toward the high reactivity of iodides as the main cause for interface instability, as they are oxidized by the MoO$_3$ substrate while bromides do not significantly react with this metal oxide. The effect of changing the cation is more subtle, where MAI is expected to degrade faster than FAI. The presence of surface oxygen vacancies is, however, vital for these reactions to occur. These mechanisms, suggested by the DFT calculations, are in excellent agreement with experimental observations made by XPS where we monitor changes in oxidation states and surface composition. Importantly, by reducing the number of oxygen vacancies on the MoO$_3$ surface via ozone treatment, we manage to reduce the reactivity of MoO$_3$ with iodide containing precursors, confirming the key role of oxygen vacancies for the decomposition process.

2. RESULTS AND DISCUSSION

In the following, we present our findings regarding the interaction between MoO$_3$ and the perovskite precursors. In section 2.1, we employ detailed DFT calculations to investigate four possible dissociation and deprotonation reactions of the different precursor molecules in contact to a pristine MoO$_3$ surface. Since there is no indication of an increased reactivity at this interface, the calculations are repeated on a surface containing oxygen vacancies, which indeed changes the reaction energies significantly. In addition, two different possible redox reactions are identified, which can lead to a reduction of Mo on the surface. In section 2.2 we compare the reactions suggested by DFT with experiments performed using XPS. Here, the interface composition as well as the oxidation states of the different species can be analyzed and associated with the different reaction pathways.

2.1. DFT Calculations. Adsorption on Pristine MoO$_3$. We investigate the adsorption of AX molecules on the pristine MoO$_3$ surface first. As is shown in Figure 1a and b, the halide ions, being negatively charged, are repelled from the negatively charged oxygen atoms that terminate the surface, while the organic cations adsorb on the substrate through hydrogen bonds that are formed between the molecules and the surface oxygen atoms. Adsorption energies can be defined as $E_{\text{ads}} = E_{\text{AX} + \text{adsorbate}} - E_{\text{AX}} - E_{\text{adsorbate}}$, where more negative energies indicate stronger adsorption. As shown in Table 1, calculated adsorption energies range from $-0.58$ to $-0.87$ eV, with I-containing molecules exhibiting a noticeably more favorable adsorption compared to Br.

This trend can be explained by the charges on the molecules, calculated with the DDEC6 method, which are also included in Table 1; for a comparison to the gas phase, we refer to Table S1. Here, the electron displacement upon the adsorption of the AX molecules on the oxide surface is an indicator of the electrostatic interaction of the molecules with the oxide. There is a charge displacement from the AX ion pairs to the MoO$_3$ substrate, as evidenced by the AX positive net charge in the range of $0.37$–$0.45e$. The larger the charge, the larger the electrostatic interaction between the AX...
molecule and the substrate and the stronger the adsorption. The slightly more favorable adsorption of the MA containing pairs compared to the FA ones can be explained by the fact that the former molecule has a larger dipole moment than the latter, interacting more strongly with the O-terminated MoO$_3$ surface. This effect can also be seen from the slightly shorter and therefore stronger N–H···O hydrogen bonds formed with the MoO$_3$ surface, which are listed in Table S2.

The chemical instability at the interface between perovskites and MoO$_3$ is often attributed to electron transfer from the perovskites to the oxide and the subsequent reduction of Mo$^{6+}$. However, it is evident from the charge difference plots in Figure 1, that the adsorption of AX on the pristine MoO$_3$ surface leaves the oxidation state of the surface Mo atoms unaffected. Instead, the electron displacement from the precursor molecules to the oxide involves the surface O atoms, whose charge becomes more negative (Figure 1a and b).

**Decomposition on a Pristine MoO$_3$**. While simple adsorption of the perovskite precursor molecules on the pristine MoO$_3$ surface does not have any significant effect on the surface, it might facilitate decomposition of the molecules. To study this, we select two possible reaction paths for MAX and FAX decomposition that have been suggested in the literature,

and we examine how adsorption of the precursor molecules to the oxide involves the surface O atoms, whose charge becomes more negative (Figure 1a and b).

Possible decomposition reactions of MAI and MABr are reviewed and discussed in detail in ref 50 where it is argued that the proton transfer reaction (reaction A1) is in competition with C–N bond breakage (reaction A2). In ref 33 it is shown that the presence of a substrate can tip the balance either in favor of the former or of the latter, depending on the substrate. In ref 51, reaction B2 is identified from experiments as a possible decomposition reaction of FAI and FABr.

We define the dissociation energies as $E_{\text{diss}} = E_{\text{fin}} - E_{\text{init}}$ where $E_{\text{fin}}$ and $E_{\text{init}}$ are the energies of the reaction product molecules and the starting reactant molecules, respectively, when adsorbed on the surface. The geometries of the reaction products and the dissociation energies are presented in Figure 2 and Table 2, respectively. For comparison, the corresponding

- **Table 1. Adsorption Energies and Electron Transfer (Characterized by Net Charge) of AX Precursors to the Pristine and Defective MoO$_3$ Surfaces**

| adsorbed species | adsorption energy (eV) | net charge (e) | A | X | AX | adsorption energy (eV) | net charge (e) | A | X | AX |
|------------------|------------------------|----------------|---|---|----|------------------------|----------------|---|---|----|
| MAI              | −0.87                  | +0.77          | −0.32 | +0.45 | −1.63 | +0.82          | −0.22 | +0.60 |
| FAI              | −0.79                  | +0.79          | −0.35 | +0.44 | −1.30 | +0.87          | −0.24 | +0.63 |
| MABr             | −0.62                  | +0.76          | −0.39 | +0.37 | −1.65 | +0.82          | −0.29 | +0.53 |
| FABr             | −0.58                  | +0.79          | −0.42 | +0.37 | −1.34 | +0.87          | −0.30 | +0.57 |

*The total net charge of AX in gas phase is 0. The positive net charge of AX adsorbed on oxides indicates electron transfer from AX to the surface.

The deprotonation reaction is also easier for MAX than for FAX molecules, which is consistent with the pk$_a$ of MA being lower than that of FA (in water 10.66 versus 12.52$^{33}$). It should be also be noted that, as HI is a slightly stronger acid than HBr (pk$_a$ values in water −10.0 versus −9.0),$^{33}$ one expects the deprotonation reaction for ABr molecules to be slightly easier than for AI molecules. Table 2 shows that this is indeed the case, but the effect for free-standing molecules is very small. The interaction with the substrate plays a larger role, see below.

![Figure 2. Atomistic representations of the products of reactions A1, A2, B1, and B2 for MAI and FAI adsorbed on a MoO$_3$ surface. Top row shows pristine surface and bottom row defective surface with one oxygen vacancy (at front right). A similar geometry applies for MABr/ FABr. Note that HCN (product of reaction B2) is not presented here as it leaves the surface of MoO$_3$. The adsorbed starting reactant molecules are presented in Figure 1.](https://doi.org/10.1021/acsami.1c02847)
The positive reaction energies agree with the observed stability of the AX compounds, whose dissociation to gas phase products is entropy-driven, and only occurs at elevated temperatures. Intriguingly, all reactions seem to be further suppressed on the pristine MoO₃ surface. This is evidenced by the significantly increased energies for all reactions, now ranging from 0.92 to 1.59 eV. We note that for FAX the dissociation energies are slightly decreased, but they are still much larger than 1 eV, indicating that these reactions are unlikely to occur. The unfavorable decomposition of the AX molecules on the pristine MoO₃ is related to the small adsorption energies, and thus weaker electrostatic interaction, of the resulting uncharged reaction products (ranging from −0.04 to −0.25 eV) compared to the adsorption of the intact precursors (−0.58 to −0.87 eV), as shown in Tables 1 and S3.

It should be noted that the deprotonation reaction has become somewhat easier for Br containing molecules, as compared to I containing molecules, whereas there is hardly any difference between the two for the free-standing molecules. We believe that this is because the product molecule HBr has a larger dipole moment than HI, which makes its electrostatic interaction with the substrate stronger, and increases its adsorption strength.

For the molecules adsorbed on surfaces it is unlikely that entropy considerations are going to change this picture significantly. At very low concentration of adsorbed molecules, reactions A₁−B₂ are of course entropy-driven. A simple estimate of the change in mixing entropy per starting molecule for reactions A₁−B₂ gives 

\[ \Delta S_{\text{mix}} = -k_B \ln x - (2 - x) \ln(1 - 2x) + (1 - 1/x) \ln(1 - x) \]

with \( k_B \) as the Boltzmann constant and \( x \) as the fraction of surface sites occupied by adsorbed starting molecules. For instance, at \( x = 1/4 \) and room temperature, this gives a contribution to the reaction free energy of \( -T \Delta S_{\text{mix}} \approx -0.05 \text{ eV} \), which is by far insufficient to counteract the large positive dissociation energies.

Adsortion and Decomposition on a Defective MoO₃ Surface. So far, our results indicate that the pristine MoO₃ surface is not reactive. However, surface defects, such as oxygen vacancies, are expected to be present on any metal oxide at a concentration of a few percent. These vacancies will also be present on MoO₃, which will be confirmed by XPS measurements shown in section 2.2 below. Accordingly, we continue our DFT study of reactions A₁−B₂, this time with an O vacancy on the MoO₃ surface. In this case, the adsorbed AX molecule breaks up into the organic cation \( \text{A}^+ \) and the halide anion \( \text{X}^− \) (Figure 1c,d). The organic cation interacts weakly with the surface O atoms, similar as in the case of the pristine surface, but the halide anion takes the place of the O vacancy, where it has a strong interaction with the exposed Mo atom underneath. The result is a notable increase in adsorption energy, which doubles for some of the molecules compared to the pristine surface (Table 1). Differences in adsorption energies come mostly from the choice of organic species. Like we argued for adsorption on the pristine surface, MA has a larger dipole moment and shorter hydrogen bonds to the metal oxide, leading to stronger adsorption compared to FA.

In contrast to the pristine surface, the presence of an O vacancy on the MoO₃ surface lowers all energies of reactions A₁−B₂ significantly compared to either the free-standing molecules or the molecules adsorbed on the pristine MoO₃ surface (Table 2). This happens because all reaction products interact much more strongly with the defective MoO₃. As shown in Figure 2, the neutral MA, NH₄, and FA molecules (products of reactions A₁, A₂, and B₁) occupy the position of the O vacancy, acting as Lewis bases with their N atoms forming bonds with the exposed Mo atom underneath. Among the products of reaction B₂ is NH₂X, which splits up into an NH₄⁺ cation adsorbed on the surface, and an X⁻ anion occupying the position of the O vacancy. As this latter situation is not so different from that of the starting products (Figure 1d), the energy of reaction B₂ is not decreased to the same extent as the other reactions.

The adsorption energies of all species involved in reactions A₁−B₂ are summarized in Table S3. Clearly, in comparison to the pristine MoO₃ surface, both the deprotonation and the dissociation of AX precursors are promoted in the presence of oxygen vacancies. As discussed above, deprotonation is easier for Br than for I containing species, because the product molecule HBr has a larger dipole moment than HI, making its electrostatic interaction with the substrate stronger, and increasing its adsorption strength. In contrast to the free-standing molecules, deprotonation of FA containing molecules has also become easier than that of MA containing molecules. This reflects the stronger interaction of the neutral (Lewis base) FA molecule with the Mo atom in the substrate that is left exposed by the oxygen vacancy. Dissociation of MA containing species is easier than that of FA containing ones, because of its weaker C−N bond, as discussed above.

Like for the pristine case, we expect entropy effects for these surface reactions to be small. For a fixed O vacancy configuration on the surface, simple mixing entropy for reactions A₁, A₂, and B₁ is absent, as the nitrogen containing product, MA, NH₄, or FA, always adsorbs at the O vacancy sites. In case of reaction B₂ there will be a limited mixing entropy effect as discussed above, which is however insufficient to make this reaction favorable. Nevertheless, reactions with energies \( \lesssim 0.1 \text{ eV} \), Table 2, may be somewhat stabilized by entropy effects.

In conclusion, adsorption of an AX molecule on a defective MoO₃ surface results in X⁻ ions occupying O vacancy sites where they bind to Mo atoms. In the case of MAX, there is a possibility that a MA molecule dissociates, leaving NH₄ to...
occupy the O vacancy sites. The reaction energy being close to zero suggests that the Lewis base NH$_3$ can be easily exchanged with another Lewis base such as a X$^-$ ion coming from a second AX molecule. Deprotonation leads to neutral MA or FA molecules occupying O vacancy sites, which, following a similar reasoning, can be exchanged with X$^-$.

**Redox Reaction 1.** While the above reactions might lead to precursor decomposition, they do not explain the degradation of MoO$_3$ that has been observed experimentally. As MoO$_3$ is an oxidizing agent and halide ions can be potentially reduced, this opens possibilities for redox reactions between the metal oxide and the AX adsorption/dissociation products. In Figure 3, we illustrate how HX molecules adsorbed on the surface of MoO$_3$ can lead to the formation of X$_2$ and the creation of an O vacancy (V$_O$), according to the following reaction:

$$2HX \rightarrow X_2 + H_2O + V_O$$  \hspace{1cm} (R1)

As before, we assume that all molecules are adsorbed on the surface; see Figure 3. The calculated reaction energies are $-0.11$ and $+0.80$ eV for HI and HBr, respectively. The disparity can be explained from the facts that HI is a somewhat stronger Bronsted acid than HBr (pK$_a$ HI in water $-1.00$ versus HBr $-9.0$)\textsuperscript{54}, but, more importantly, reduction of iodides is easier than that of bromides (the standard reduction potential of I$_2$ to 2I$^-$ is 0.54 V, whereas that for Br$_2$ to 2Br$^-$ is 1.07 V\textsuperscript{52}). Therefore, reaction R1 is likely to happen for HI but unlikely for HBr.

Notably, reaction R1 can take place without the presence of any oxygen vacancy, instead a vacancy is created in the process. This leads to the reduction of MoO$_3$, as can be seen clearly when comparing the calculated density of states (DOS) of a pristine MoO$_3$ surface to that of a surface with an O vacancy, as shown in Figure 4. The DOS of a pristine surface (Figure 4a) is typical for a metal oxide semiconductor/insulator, with the top of the valence band being dominated by O p states, and the bottom of the conduction band by Mo d states, respectively, which is consistent with the Mo species being fully oxidized to Mo$^{6+}$. Upon the creation of an oxygen vacancy, we observe the appearance of two peaks within the bandgap, with a mixed Mo–O character (Figure 4b). Judging from the lack of dispersion of these peaks, the corresponding states are localized. It should be noted that, in agreement with ref 58, creation of an O vacancy leads to a sizable local geometry distortion in the lattice. A spatially resolved DOS shows that the two gap states are localized around this geometry distortion (Figure S4), and particularly around two Mo atoms at the center of the distortion. The two gap states are each occupied by a single electron (spin-up, Figure 4b), which in chemical terms corresponds to a reduction of two Mo atoms from Mo$^{6+}$ to Mo$^{5+}$.

This situation described here represents a neutral O vacancy defect, which has two donor levels in the bandgap. Acting as a double donor, the maximum charge of an oxygen vacancy is 2+, which indeed has been found as the most stable charge state in previous work.\textsuperscript{58}

**Redox Reaction 2.** As discussed above, the creation of an O vacancy reduces MoO$_3$, but there is another process that can even further reduce the defective oxide. The presence of an O vacancy V$_O$ on the surface of MoO$_3$ leaves a Mo atom exposed and creates an adsorption site for the halogen X of a precursor molecule, X–V$_O$, as discussed above (Figure 1c,d). The
adsorption of a second AX molecule near this site can trigger a catalytic redox reaction

\[ AX + X - V_O \rightarrow A^+ + X_2 + V_O + \varepsilon \]  

(R2)
as shown in Figure 3. From the reaction energies listed in Table 3, we can see that out of the four precursors, the reaction

| Table 3. Reaction Energies (eV) of the Two Redox Reactions R1 and R2* |
|---------------------------------------------------------------|
| R1: 2HX → H_2O + V_O | R2: AX + X-V_O → A^+ + X_2 + V_O + ε |
| MAI | −0.11 | MAI | −0.11 |
| FAI | −0.11 | FAI | +0.10 |
| MABr | +0.80 | MABr | +0.21 |
| FABr | +0.80 | FABr | +0.39 |

“X-V_O refers to an oxygen vacancy site occupied by a halide.

for MAI is deemed to be most favorable, followed by FAI, whereas the reactions for the Br containing species are less favorable. This finding reflects the facts that iodides are more easily oxidized than bromides, and MA^+ adsorbs more strongly on the surface than FA^+ (Table 1). Therefore, we expect the interaction of the defective MoO_3 surface with MAI to lead to the formation of I_2. The adsorption energy of I_2 on the oxide is −0.17 eV (with respect to the surface with a O vacancy and a free molecule). As the condensation energy of a I_2 molecular solid is ~0.8 eV/molecule, it is thus energetically advantageous for the I_2 molecule to leave the MoO_3 surface.

Redox reaction R2 further reduces the MoO_3 substrate, which can be seen in the DOSs for MoO_3 with the A end product of reaction R2 adsorbed and X_2 desorbed. Figure 4c shows the DOS for adsorbed MA. Similar to the oxygen vacancy (Figure 4b), there are two occupied states clearly within the bandgap, originating from the surface. Contrary to Figure 4b, Figure 4c shows a third state, with an energy just below the conduction band. This state is also occupied, hence the shift of the Fermi level from Figure 4b to c, indicating that, as a result of reaction R2, an additional electron is donated to the MoO_3 substrate.

An electron count puts the number of these additional electrons to one (per O vacancy site), as it stems from the oxidation of I_2, which becomes neutral, as the net charge of an I_2 molecule is zero. The DOS indicates that the electron transferred to the MoO_3 is somewhat localized, which would agree with the polaronic localization suggested in ref S8. Moreover, the oxide films used in experiment are likely to show some local inhomogeneity, which further promotes localization of electrons. Such localization of added electrons manifests itself in changed oxidation states, from Mo_6^6+ to Mo_3^5+, or, depending on the film inhomogeneities to Mo^4+ or Mo^3+. This is indeed the case as will be discussed in the next section.

To summarize all the above-described six reactions, oxygen vacancies on the surface of MoO_3 facilitate the decomposition of the perovskite AX precursors. The decomposition products can in turn create more oxygen vacancies, reducing the involved Mo species, from Mo_6^6+ to Mo_3^5+. Subsequently, another reaction involving the defective MoO_3 sites can further reduce to Mo_3^4+ or even lower oxidation states. The two redox reactions are accompanied by the oxidation of the involved halide species, with the creation of X_2. We propose that, upon desorption of the created X_2 species, the oxygen vacancies become available for further redox reactions, which will in turn further reduce the Mo, making the MoO_3 surface even more defective and reactive. Overall, the calculated reaction energies (Table 3) indicate that the reactivity of the AX precursors with MoO_3 decreases in the order of MAI > FAI > MABr > FABr, suggesting that the instability could be mitigated by substituting MA with FA and/or 1 with Br.

2.2. XPS Investigations. To investigate the validity of the DFT calculations, the interaction between MoO_3 and the AX precursor materials was investigated using XPS to monitor the chemical species at the interfaces and changes in film composition. For this, MoO_3 films were prepared by thermal evaporation and transferred into a glovebox without air exposure. On top, thin layers (a few nm) of AX were deposited by spin coating a diluted solution (0.05 M), labeled as MoO_3/AX throughout this article. As reference, thick AX layers (>30 nm) were spin coated on an unreactive surface (PEDOT:PSS) and also measured by XPS.

As-Prepared MoO_3 Substrate. First, findings regarding the metal oxide will be discussed, specifically the Mo 3d core level signal. Even though MoO_3 can be prepared in high purity by evaporation in high vacuum conditions, we find that the core level signal exhibits additional reduced oxidation states besides the expected Mo_6^6+, as seen in Figure 5a. Small amounts of Mo_3^4+ and Mo^3+ can be observed in as-prepared MoO_3, ranging from 2.5–8.5% and 1.5–3.0%, respectively, as summarized Figure 6. The presence of Mo_3^4+ and Mo^3+ further reduce the Mo, making the MoO_3 surface even more defective and reactive. Overall, the calculated reaction energies (Table 3) indicate that the reactivity of the AX precursors with MoO_3 decreases in the order of MAI > FAI > MABr > FABr, suggesting that the instability could be mitigated by substituting MA with FA and/or 1 with Br.

![Figure 5. XPS core level measurements of Mo 3d peaks containing fits for the different oxidation states. The samples are (a) the as-prepared MoO_3 substrate and (b) MoO_3 substrate after spin coating the pure solvent (isopropanol/DMF) on top, while the remaining graphs show the MoO_3 substrate covered by an ultrathin layer of (c) FABr, (d) MABr, (e) FAI, and (f) MAI.](image-url)
ability to reduce Mo. Here, the precursor MAI shows a significantly higher MoO$_3$ compared to FAI, which is, although not favored over simple adsorption of the precursor molecules at the MoO$_3$ surface, still more likely to happen for MABr (reaction energy $+0.21$ eV) compared to FAI ($+0.39$ eV).

In the case of the iodide containing precursors, the negative reaction energy of $-0.11$ eV in the case of FAI and MAI, enables HI to effectively reduce Mo via redox reaction 1, forming new O vacancies and further increasing the amount of defect sites. Therefore, more surface reactions are triggered that lead to a significant higher amount of reduced Mo oxidation states, compared to the interaction with bromide precursors. The higher reactivity of MAI compared to FAI is likely related to the redox reaction 2: MAI is the only precursor where this reaction is favored over simple adsorption (negative reaction energy of $-0.11$ eV), leading to I$_3$ creation accompanied by additional Mo-reduction. For FAI, on the contrary, redox reaction 2 is not favored, but due to the very small positive reaction energy ($+0.10$ eV) still likely to occur.

Overall, in good agreement with the DFT calculations above, the XPS Mo core level signals in Figure 5 show vast differences in reactivity of the different precursors with the MoO$_3$ surface. The ability to affect the MoO$_3$ correlates with differences in reaction energy of the two possible redox reaction routes summarized in Table 3. It can be stated, that the precursor reduction potential toward Mo$^{6+}$ is most pronounced in MAI, followed by FAI, while MABr and FABr do not seem to react with MoO$_3$ in a substantial way.

Precursor Core Level Signals. Next to the effect of the AX perovskite precursors on the metal oxide’s oxidation states, it is also relevant to study the accompanying effect on the AX precursors. To this end, the relative intensities of the precursor specific core level signals of thick (unreacted) AX films are compared to the samples of ultrathin AX films on MoO$_3$. Figure 7 shows the halide signals of these pure (thick) AX layers as well as the MoO$_3$/AX interfaces. Note that these spectra have been normalized to the intensity of the nitrogen signal to be able to directly compare layers with different thicknesses and therefore different overall signal intensities. This way, a loss of the halide species relative to nitrogen due to redox reactions can be directly seen by changes in signal height. The fits for N 1s are shown in Supporting Information Figure S7. The carbon core levels could not be reliably fitted due to substrate and/or solvent signals superimposing on the signal.

When comparing the bromide signals after contact to MoO$_3$ (Figures 7b,d) with the signals from the precursor layers (Figures 7a,c), it is clear that the film stoichiometry (N to Br ratio) is not strongly affected; around 80% of bromide remains present in the samples, as can be seen in Table 4. No additional peaks and no changes in FWHM are observed, which would indicate the presence of additional oxidation states (see the Experimental section for peak fitting procedure). Therefore, no bromide-based decomposition products can be detected on the sample surface. This observation is in excellent agreement with Figure 5, where

Figure 6. Relative content of Mo oxidation states of the as-prepared MoO$_3$ substrate, MoO$_3$ after the interaction with the solvent, and after the deposition of an ultrathin precursors layer on top.
Br 3p signal

![Br 3p signal](image)

I 3d3/2 signal

![I 3d3/2 signal](image)

Figure 7. XPS core level measurements. Turquoise shaded fits: Br 3p peaks of (a) an unreacted thick FABr layer, (b) an ultrathin layer of FABr on MoO$_3$, (c) an unreacted thick MABr layer, and (d) an ultrathin layer of MABr on MoO$_3$. Blue shaded fits: I 3d3/2 peaks of (e) an unreacted thick FAI layer, (f) an ultrathin layer of FAI on MoO$_3$, (g) an ultrathin layer of FAI on ozone treated MoO$_3$, (h) an unreacted thick MAI layer, (i) an ultrathin layer of MAI on MoO$_3$, and (j) an ultrathin layer of MAI on ozone treated MoO$_3$.

Table 4. Halide Content of the Thick Unreacted AX Precursor Layers and the Precursors Spin Coated As Ultrathin Layers on MoO$_3$ Substrate

| Substrate | MoO$_3$/FAI | MoO$_3$/FAI | MoO$_3$/MABr | MoO$_3$/FAI | MoO$_3$/FAI |
|-----------|-------------|-------------|--------------|-------------|-------------|
| MAI       | 1.0         | 1.0         | 2.0          | 2.0         | 1.0         |
| FAI       | 1.1         | 0.5         | 1.0          | 0.6         | 0.9         |
| MABr      |             |             |              |             |             |
| FAI       | 0.9         | 0.7         | 1.1          | 0.9         |             |

**Note:** For MAI and FAI, ozone treated MoO$_3$ substrates are included (note, values are normalized to the amount of N on the surface, which is set to be 1.0 for MA and 2.0 for FA).

be observed here. Indeed, a large decrease of the iodide XPS signals is observed for MAI and FAI (compare Figure 7f and i with e and h), suggesting that a volatile iodine species, most likely I$_2$, as a product of redox reactions, is formed. This effect is more pronounced in MAI, where only 50% of the iodide species remain on the sample surface, while the loss is slightly less pronounced but still significant in FAI (~60% of expected intensity found). Since no neutral halide signal is found at higher binding energies, it can be assumed that I$_2$ readily leaves the sample surface, as predicted by the DFT calculations.

Overall, XPS shows that the tendency of the materials to form volatile X$_2$ follows the order MAI $\gg$ FAI $>$ MABr $>$ FABr. This trend is in agreement with the previously established ability of the AX precursors to reduce MoO$_6^{2-}$ to lower oxidation states, as well as the results gained by DFT calculations.

**Role of Deposition Order.** Similar experiments, using a reversed deposition order in an in situ experiment, were also conducted in order to test if MoO$_3$ deposited on top of AX leads to comparable results. For this, 2.5 nm of MoO$_3$ was evaporated on top of the different 30 nm thick AX layer; the measurements of these AX/MoO$_3$ interfaces can be found in the Supporting Information, Figures S5$-$S7. Intriguingly, the deposition order seems to play only a minor role in the interface reactivity. Compared to the solution processed interfacial presented above, a slightly higher fraction of reduced Mo species was observed in some cases when MoO$_3$ was evaporated on top of the precursors (up to 20%, see Figure S5) and the overall decrease in the halide signals is also slightly higher here (up to 10%, Figure S5 and Table S5 in SI). Importantly, the overall trends regarding the reactivity remain the same. The increased reactivity is likely due to the fact that the evaporated MoO$_3$ carries a certain amount of thermal energy when impacting on the precursor surface, since the evaporation temperature of MoO$_3$ is above 600 °C.

**Surface Passivation.** In the previous section we found that avoiding iodide containing precursors at the interface to MoO$_3$ could be an option to bypass the commonly observed interfacial instability. In addition, the DFT calculations suggest that another possible route could be the elimination of oxygen vacancies. Without these vacancies, the energy barrier of the deprotonation reaction is high and HX should not be generated; hence redox reaction 1 cannot take place. Similarly, for redox reaction 2, O$_{vac}$ are needed as an adsorption site for the halogen to initiate the reaction. Reducing the number of oxygen vacancies on the MoO$_3$ surface should therefore decrease the reactivity of the iodide containing precursors with MoO$_3$. To verify this assumption, the surface of MoO$_3$ layers was UV/ozone treated. Looking at the resulting Mo 3d core level signal in Figure 8a, it is obvious that the amount of lower oxidation states in the ozone treated MoO$_3$ substrate is significantly reduced (from 8.4% Mo$^{5+}$ and 2.8% Mo$^{4+}$ in as prepared MoO$_3$ to 1.3% Mo$^{5+}$ and 1.8% Mo$^{4+}$ in ozone treated MoO$_3$).

On top of these pretreated surfaces, ultrathin layers of either FAI or MAI were spin coated, similar to the experiments presented above in Figure 5. The Mo core level signals in contact with the precursors are shown in Figures 8b,c. It can clearly be seen that upon contact the amount of reduced Mo species is significantly lower compared to the experiments on untreated MoO$_3$ layer (see Figure 5e and f). Notably, the amount of reduced Mo oxidation states for MoO$_3$(ozone)/FAI is now as low as the bromide containing precursors (FABr and no significant interaction between Br containing precursors and MoO$_3$ was found.

Since a pronounced reactivity toward Mo was found for iodide containing precursors, more changes can be expected to...
In this work, we investigate the interaction of MoO$_3$ with different perovskite precursors using a combination of DFT calculations and XPS measurements. The calculations indicate that a pristine MoO$_3$ surface is unlikely to decompose the perovskite precursors and oxygen vacancies are proposed as reaction centers for such processes. The existence of vacancies in the range of a few percent in as-deposited MoO$_3$ is demonstrated via XPS investigations as evidenced by the presence of Mo atoms with reduced oxidation states. We suggest that reaction products of the precursor decomposition may create additional oxygen vacancies, reducing MoO$_3$ even further. In addition, we propose that oxygen vacancy sites are also involved in oxidizing the precursor halide molecules directly, adding to the reduction of the oxide. In the proposed scenario, reduction of MoO$_3$ is accompanied by oxidation of the halides. Interestingly, both from the calculations and from experiment, I is found to be much more reactive than Br.

XPS measurements show that bromine containing precursors do not significantly affect MoO$_3$, while iodide containing organic cations (MAI and FAI) strongly reduce the metal oxide. This is accompanied by a significant loss of iodine, which forms a volatile compound (I$_2$). In addition, both DFT calculations and XPS measurements lead to the same order in precursor reactivity, which is MAI $>$ FAI $>$ MABr $>$ FABr. Our results suggest that avoiding I at the interface with MoO$_3$ will be an effective way to reduce the interfacial instability known for this metal oxide. In addition, we are able to show that lowering the number of oxygen vacancies by an ozone treatment also leads to an improved stability of the iodide containing precursors on the MoO$_3$ surface.

Overall, our investigations on these precursor materials show that the interface reactivity of a metal oxide toward an adjacent perovskite layer is strongly affected by the choice of organic cation and halide, as well as the surface defect density. It is therefore worth not disregarding metal oxide layers, such as MoO$_3$, just because of reports of instability toward certain perovskite compositions.

4. COMPUTATIONAL AND EXPERIMENTAL DETAILS

Computational Details. Density functional theory calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna Ab-Initio Simulation Package (VASP). The electronic exchange-correlation interaction was described by the functional of Perdew, Burke, and Ernzerhof (PBE) within the generalized gradient approximation (GGA). Energy and force convergence criteria of $10^{-5}$ eV and $10^{-3}$ eV/Å, respectively, were used in all calculations.

MoO$_3$ is a layered material that comprises a stack of bilayers, where each bilayer consists of corner-connected and edge-shared MoO$_6$ octahedra, and the bonding between the bilayers originates from weak van der Waals forces. Due to the weak interlayer interactions, a single bilayer is sufficient for the study of the MoO$_3$ surface. For all the calculations a (3 × 3) bilayer and a vacuum region of 12 Å were used. The calculations were performed with a (2 × 2 × 1) Monkhorst-Pack k-point grid and a kinetic energy cutoff of 500 eV. A dipole correction was employed to avoid interaction between periodic images. For the density of states calculations a (4 × 4 × 1) Monkhorst-Pack k-point grid was used along with the DFT+U method as proposed by Dudarev et al. Following the literature, a value of 6.3 eV was used for the U/J parameter.

The adsorption energies of the perovskite precursors and their dissociation products on the MoO$_3$ surface were calculated as

$$E_{ads} = E_{MoO_3/adsorbate} - E_{MoO_3} - E_{adsorbate}$$

where $E_{MoO_3/adsorbate}$, $E_{MoO_3}$ and $E_{adsorbate}$ are the DFT total energies of MoO$_3$ with adsorbed species, the clean MoO$_3$ surface and the adsorbate molecules, respectively. The net atomic charges and bond orders were calculated using the density derived electrostatic

| Precursors Layer | MAI | MoO$_3$(ozone)/MAI | FAI | MoO$_3$(ozone)/FAI |
|------------------|-----|--------------------|-----|--------------------|
| N                | 1.0 | 1.0                | 2.0 | 2.0                |
| I                | 1.1 | 1.2                | 1.0 | 1.1                |

*Note, values are normalized to the amount of N on the surface, which is set to be 1.0 for MA and 2.0 for FA.*
and chemical (DDEG6) method. For the charge difference plots, the charge density of the clean MoO₃ monolayer and that of the free-standing molecules, both in the adsorption geometry, were subtracted from the charge density of the MoO₃ with adsorbed species.

**Experimental Details.** MoO₃ films were prepared on ITO substrates, onto which 31 nm of MoO₃ (Alfa Aesar, 99.95% metal basis) layer were evaporated in a vacuum chamber (base pressure: p < 7 × 10⁻⁸ mbar) which is directly attached to the measurement system. A deposition rate of 0.1 Å/s was recorded by a calibrated quartz crystal monitor (QCM) using 4.69 g/cm² as the density for MoO₃. The MoO₃ substrates were then transferred under a nitrogen atmosphere into the preparation glovebox, where diluted 0.05 molar precursor solutions were spin coated (spin rate 1500 rpm for 45 s). Afterward, the samples were annealed at 80 °C for 40 min and then transferred under nitrogen atmosphere back into the analysis chamber for XPS measurements.

For the thick precursor layers, as well as the reversed deposition order presented in the SI, an aqueous solution of PEDOT:PSS (Clevios PV P VP Al 4083, Heraeus) was spin coated at 2500 rpm onto ozone-treated inch-sized ITO substrates and annealed at 150 °C for 10 min. The thick films of MAI, FAI, MABr, and FABr (all purchased from Great Cell Solar, purity >99.99%) were prepared via spin coating under nitrogen atmosphere in a glovebox. For that, in case of MAI, FAI, and FABr, 5 × 110 μL of a 0.5 molar precursor solution in 98% isopropanol (Honeywell, CHROMASOLV LC-MS, 99.9%) and 2% DMF (Sigma-Aldrich, HPLC grade, ≥99.9%), and in case of MABr a 0.5 molar solution in 75% isopropanol and 25% DMF, were spin coated on top of the PEDOT:PSS using the same conditions and solvent ratios as mentioned above. Afterward, the samples were annealed at 80 °C for 40 min. The inch-sized samples were cut into four pieces and transferred to a vacuum chamber under nitrogen atmosphere. Two of these pieces were investigated directly via XPS. On top of the other two samples, a 2.5 nm MoO₃ layer was evaporated and measured in situ.

The photoelectron spectroscopy measurements were performed on a custom designed multichamber UHV system at a base pressure of <10⁻¹⁰ mbar, using a Phoibos 100 hemispherical analyzer (Specs). The Fermi edge of gold substrates, cleaned via surface sputtering, was used for calibrating the electron binding energy scale. XPS measurements were done using a Mg Kα X-ray source (hv = 1252.6 eV) at a pass energy of 20 eV for nitrogen, iodine, and bromine peaks. For the investigating the molybdenum signals, a pass energy of 10 eV was used to improve the overall energy resolution of the measurement.

**Peak Fitting.** For investigating the XPS peaks the program XPSPEAK 4.1 was used, using a Shirley background for all element peaks. Parameters for Lorentzian to Gaussian ratio (L-G) and FWHM were kept identical for each specific element (L-G for 1 d₃/₂ = 45, Br 3d = 30, N 1s = 30, and Mo 3d = 23; FWHM (±0.05 eV) for 1 d₃/₂ = 1.75 eV, Br 3d = 2.6 eV, N 1s = 1.65 eV and Mo 3d = 1.26 eV) for all fits. Sample compositions were calculated using the respective peak areas after background subtraction and correction by the respective RSF values (calibrated for the system). Afterward, the received areas of the halide signals were normalized to the areas of the charge density of the clean MoO₃ surface basis) layer were evaporated in a vacuum chamber (base pressure: p < 7 × 10⁻⁸ mbar) which is directly attached to the measurement system. A deposition rate of 0.1 Å/s was recorded by a calibrated quartz crystal monitor (QCM) using 4.69 g/cm² as the density for MoO₃. The MoO₃ substrates were then transferred under a nitrogen atmosphere into the preparation glovebox, where diluted 0.05 molar precursor solutions were spin coated (spin rate 1500 rpm for 45 s). Afterward, the samples were annealed at 80 °C for 40 min and then transferred under nitrogen atmosphere back into the analysis chamber for XPS measurements.

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**Author Contributions**

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**Notes**

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Additional DFT results (bond order, net charges, adsorption energies), reaction schemes for the pristine MoO₃ (surface, DOS calculations) as well as additional XPS measurements (reversed deposition order, nitrogen peaks) (PDF)
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