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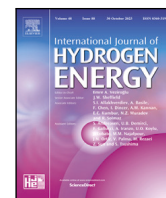
Ricciarelli, D., Mosconi, E., Wiktor, J. et al (2024). Electron bipolarons at the  $\text{DMASnBr}_3$ -water interface: Effect on the photocatalytic hydrogen production. *International Journal of Hydrogen Energy*, 58: 863-871.  
<http://dx.doi.org/10.1016/j.ijhydene.2024.01.268>

N.B. When citing this work, cite the original published paper.



Contents lists available at ScienceDirect

## International Journal of Hydrogen Energy

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Electron bipolarons at the DMASnBr<sub>3</sub>–water interface: Effect on the photocatalytic hydrogen production

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## ARTICLE INFO

## Keywords:

Water-stable metal halide perovskites  
 Photocatalysis  
 pH-dependent surface chemistry  
 Small electron bipolarons  
 Ab initio molecular dynamics  
 Energy levels alignment

## ABSTRACT

In this article, we report on advanced molecular dynamics simulations of the atomistic DMASnBr<sub>3</sub>–water interface, which, coupled with a grand-canonical formulation of adsorbates and defects, elucidate the surface chemistry and reactivity of this novel water-stable perovskite and highlight the role of small electron bipolarons in photocatalytic hydrogen production. We find that the extremely acidic nature of the surface Br atoms does not allow for significant adsorption of protons at the interface under charge-neutral conditions. However, when electrons are accumulated on the surface, the formation of a small electron bipolaron in the form of a Sn-Sn dimer provides the required electron localization to drive adsorption of H, which is assimilated on surface Sn atoms as hydride. Finally, we estimate a favourable alignment between the bipolaron energy level and the H<sup>+</sup>/H<sub>2</sub> redox level, which suggests the occurrence of a feasible route for hydrogen evolution, bypassing the common reaction mechanism.

## 1. Introduction

Photocatalytic water splitting at the semiconductor–water interface may support the production of clean fuel by mimicking natural processes occurring in photosynthesis [1–12]. However, notwithstanding the large efforts deployed in the last decade [13–18], an ideal photocatalyst has not been found yet. In fact, a material should meet a vast number of requirements to be a candidate photocatalyst. Its band gap  $E_g$  should be comprised between 1.23 and 3 eV, in order to straddle the hydrogen reduction and the water oxidation redox levels in water, while being able to absorb the largest fraction of the visible spectrum [4,6]. A long lifetime and high mobility of the charge carriers is also desirable [19–21], along with a strong defect tolerance [22,23]. Moreover, the valence (VB) and conduction band (CB) edges should be properly aligned with respect to the redox levels of liquid water, to ensure that charge-transfer processes at the heterogeneous interface are thermodynamically favourable [24–28]. Finally, to avoid or

minimize the addition of protective layers [29,30] and/or expansive cocatalysts [31], an excellent photocatalyst should be stable in aqueous environment and dissociate water on its surface [26,27,32,33].

The extensive search for the optimal photocatalyst, while encompassing a plethora of innovative materials including e.g. nanostructured [34,35], 2D [36,37], and magnetic materials [38], has for long excluded the most intriguing class of novel semiconductors, metal halide perovskites (MHPs), which are easily synthesized and display opto-electronic properties rivalling those of state-of-the-art semiconductors [39–46]. Besides, MHPs are generally defect tolerant [47–49] and the band gap and the band edges can be easily tuned by varying the composition in the ABX<sub>3</sub> formula, with different inorganic or inorganic A-site cations (e.g. Cs<sup>+</sup> and CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>), halides (I, Br, Cl) and metals (Pb, Sn, Ge). Such a flexibility permits to easily attain, via material design, the alignment with the redox potentials in aqueous solution for the desired reactions [50,51].

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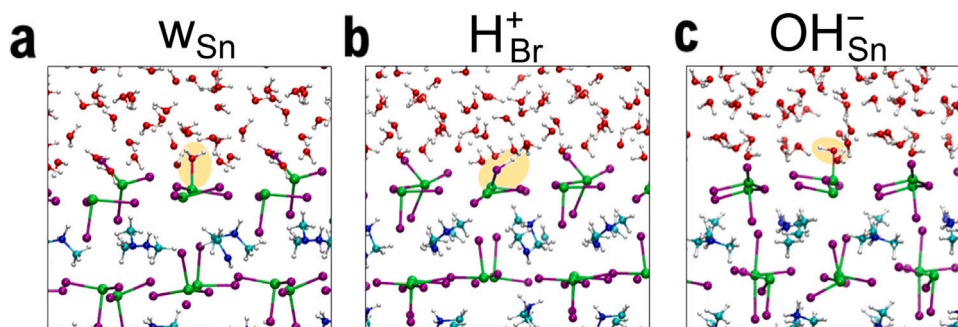
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<https://doi.org/10.1016/j.ijhydene.2024.01.268>

Received 8 September 2023; Received in revised form 17 January 2024; Accepted 21 January 2024

Available online 30 January 2024

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**Fig. 1.** Stick&ball representation (side-view) of a structural configuration of (a) an adsorbed  $\text{H}_2\text{O}$  molecule, (b) an adsorbed  $\text{H}^+$ , (c) an adsorbed  $\text{OH}^-$  at the  $\text{DMASnBr}_3(001)$ -water interface. Sn atoms in green, Br in purple, O in red, and H in white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Two main drawbacks have hitherto hindered the efforts to introduce MHPs to photocatalysis: (i) their poor stability upon moisture and water exposure [52–55], and (ii) the large performance and stability gap between MHPs containing lead, which is toxic, and more environmental-friendly lead-free materials [56–63]. For these reasons, only in the last years, MHPs have emerged in heterogeneous photocatalysis as a possible alternative to traditional semiconductors. The first attempts to employ MHPs in photocatalytic  $\text{H}_2$  production have been conducted either immersing the material in highly concentrated halogen acid solutions, to limit material degradation, which is usually initiated by halogen loss [47,64], or protecting the photocatalyst with water-resistant overlayers/encapsulation [51,65,66]. Nevertheless, these strategies, allowing for a proper evaluation of MHPs activity, reduce the feasibility of related devices.

Very recently, encouraging results have been obtained for Bi, Ge, and Sn perovskites possessing both significant water stability and good photocatalytic properties [67–72]. In particular, dimethylammonium tin bromide ( $\text{DMASnBr}_3$ ) with its suitable band gap, 2.85 eV [69,73], and its band edges well positioned with respect to the redox levels of liquid, has proved to be particularly promising with measured rates of hydrogen production exceeding  $1700 \mu\text{mol g}^{-1} \text{h}^{-1}$  in composites with  $\text{g-C}_3\text{N}_4$  [69,74]. In this context, it has been established that strong electron localization associated with bipolaron formation is recurrent in tin halide perovskites (THPs) with binding energies correlated with the energy level of the CB [59,75,76]. Furthermore, bipolaron formation at the surface is predicted to be key in the hydrogen evolution reaction at the surface of THPs [76]. However, an in-depth comprehension of the surface chemistry is still lacking [77]. In fact, while the study of atomistic interfaces has unveiled the reason beyond the unprecedented water stability shown by  $\text{DMASnBr}_3$  [78], the acid–base chemistry, which is fundamental in assessing the potential photocatalytic activity of candidate semiconductors [27], has not been analysed yet. Furthermore, even though the formation of electron bipolarons has been demonstrated for the bulk material and bare surfaces [75,76], a characterization of the electronic structure and associated energy levels on the more realistic interface model is mandatory to attain a more accurate depiction of the electron transfer processes possibly occurring in photocatalytic  $\text{H}_2$  production.

In this article, we study the atomistic  $\text{DMASnBr}_3$ -water interface at room temperature via *ab initio* molecular dynamics (MD) simulations, which are employed to calculate free energies within a grand canonical formulation of adsorbates and defects at the heterogeneous interface. The achieved results provide fundamental insights into the surface chemistry and reactivity of this material and expand the recent but growing literature of polaronic effects in heterogeneous photocatalysis. We first study the pH-dependent surface chemistry of the  $\text{DMASnBr}_3$ -water interface in absence of photogenerated charges and discover that the perovskite surface is decidedly inert with protons being hardly adsorbed in a wide range of pH values. However, small electron bipolarons occurring via the formation of a Sn–Sn bond are found to

provide the much-needed charge localization to induce H adsorption as surface hydride. Finally, from the alignment of the band edges and the polaronic energy level of  $\text{DMASnBr}_3$  with the redox levels of liquid water, we evince a favourable energetics towards photocatalytic hydrogen production, within a reaction path alternative to the traditional mechanism.

## 2. Computational details

We carry out DFT Born–Oppenheimer molecular dynamics (MD) simulations of the atomistic interface between liquid water and  $\text{DMASnBr}_3$  with the CP2K suite of programs [79]. Simulations are carried out in the NVT ensemble. The target temperature, controlled with a Nose–Hoover thermostat [80,81], is set at 350 K, in order to achieve liquid-like behaviour and to approximately take into account nuclear quantum motion [82]. A time-step of 0.48 fs is employed to properly sample the fast stretching modes of liquid water. Production runs of 8–10 ps are preceded by an equilibration run of 2 ps. Simulations are performed with the rVV10 functional [83,84], to correctly include non-local electron correlation. Goedecker–Teter–Hutter pseudopotentials are used to account for core–valence interactions [85]. We employ the MOLOPT double- $\zeta$  polarized basis sets [86] and a cut-off of 600 Ry for the expansion of the electron density in plane waves. The choice of a semilocal functional is here motivated by the benchmark carried out in a previous study, in which it has been shown that the energetics of conduction band states and of localized electrons is close to that achieved with more computationally expansive hybrid functionals [76]. We have further verified this by re-evaluating specific total-energy differences at the hybrid-DFT [87–94] level (cf. Supplementary Information).

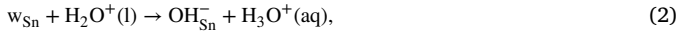
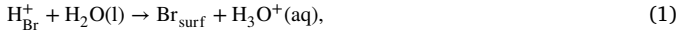
## 3. Results and discussion

We first consider a neutral  $\text{DMASnBr}_3(001)$ -water interface. This is constructed as  $2 \times 2$  orthorhombic supercell [ $a = 12.274$ ,  $b = 12.071$ , and  $c = 47.500 \text{ \AA}$  with  $a$  and  $b$  corresponding to experimental values [69], cf. Figure S1 (a)]. The model includes 72  $\text{H}_2\text{O}$  molecules, corresponding to the experimental density of liquid water [cf. Figure S1 (b)]. Such a model has been extensively characterized in a previous study [78] and features a  $\text{SnBr}_2$ -terminated slab, with water molecules being molecularly adsorbed on the semiconductor interface through a Sn–O bond of  $\sim 2.40 \text{ \AA}$  and only weakly interacting with surface Br sites as illustrated by the Sn–O and H–Br radial distribution functions [cf. Figure S1 (c)]. We note that the use of a  $\text{SnBr}_2$ -terminated slab is here motivated by the higher stability that  $\text{BX}_2$  surfaces exhibit with respect to those featuring an AX coverage [54].

Starting from the neutral  $\text{DMASnBr}_3(001)$ -water interface [ $w_{\text{Sn}}$ , cf. Fig. 1(a)], we carry out molecular dynamics (MD) simulations (i) where an extra proton is added close to a surface Br atom ( $\text{H}_{\text{Br}}^+$ ) [cf. Fig. 1(b)] and (ii) in which an adsorbed  $\text{H}_2\text{O}$  molecule is replaced by an hydroxyl ion ( $\text{OH}_{\text{Sn}}^-$ ) [cf. Fig. 1(c)]. For  $\text{H}_{\text{Br}}^+$  we estimate an average H–Br distance

of 1.70 Å,  $\sim 0.3$  Å longer than HBr bond length. A small reduction of the Sn–O bond ( $\sim 0.2$  Å) is observed when an adsorbed water molecule is replaced by an hydroxyl ion [cf. Fig. 1c], as a consequence of a stronger Sn–O interaction.

To evaluate the pH-dependent surface chemistry at the semiconductor–water interface, we calculate the acidity of the surface sites. To this end, we consider the adsorbed species being subject to following acid–base equilibria:



which represent the acidic dissociation of the adsorbed proton and water molecule, respectively. The associated acidic constants read as follows:

$$K_a(\text{H}_{\text{Br}}^+) = \frac{[\text{Br}_{\text{surf}}][\text{H}_3\text{O}^+(\text{aq})]}{[\text{H}_{\text{Br}}^+]}, \quad (3)$$

$$K_a(\text{w}_{\text{Sn}}) = \frac{[\text{OH}_{\text{Sn}}^-][\text{H}_3\text{O}^+(\text{aq})]}{[\text{w}_{\text{Sn}}]}, \quad (4)$$

and are here calculated with a grand-canonical formulation of adsorbates at the interface [27,32,82,95–97], which allow to express the free-energy differences of the reactions by combining MD simulations with the thermodynamic integration method [98,99]. In particular, the acidity of an adsorbate can be expressed in terms of the difference between its deprotonation free energy and that of the aqueous hydronium cation [27,32], the latter hence acting as a reference:

$$\text{p}K_a(\text{H}_{\text{Br}}^+) = \frac{\Delta_{\text{dp}}G(\text{H}_{\text{Br}}^+)}{\ln 10 \cdot k_{\text{B}}T} - \log c_0, \quad (5)$$

$$\text{p}K_a(\text{w}_{\text{Sn}}) = \frac{\Delta_{\text{dp}}G(\text{w}_{\text{Sn}})}{\ln 10 \cdot k_{\text{B}}T} - \log c_0. \quad (6)$$

In Eqs. (5) and (6),  $\Delta_{\text{dp}}G(\text{H}_{\text{Br}}^+)$ , and  $\Delta_{\text{dp}}G(\text{w}_{\text{Sn}})$  are hence the free energy changes associated with deprotonation adsorbed proton and adsorbed water molecule, respectively, referred to that of the aqueous hydronium cation, i.e. the free energies of reactions (1) and (2).  $k_{\text{B}}$  is the Boltzmann's constant and  $c_0$  is the number of water moles in 1 L of liquid water (55.5 mol/dm<sup>3</sup>).  $\Delta_{\text{dp}}G(\text{H}_{\text{Br}}^+)$  and  $\Delta_{\text{dp}}G(\text{w}_{\text{Sn}})$  are defined as [27,32]:

$$\Delta_{\text{dp}}G(\text{H}_{\text{Br}}^+) = \Delta_{\text{dp}}A(\text{H}_{\text{Br}}^+) - \Delta_{\text{dp}}A(\text{H}_3\text{O}^+) - \Delta_{\text{zp}}E(\text{H}_{\text{Br}}^+) + \Delta_{\text{zp}}E(\text{H}_3\text{O}^+) + \Delta V_{\text{w}}, \quad (7)$$

$$\Delta_{\text{dp}}G(\text{w}_{\text{Sn}}) = \Delta_{\text{dp}}A(\text{w}_{\text{Sn}}) - \Delta_{\text{dp}}A(\text{H}_3\text{O}^+) - \Delta_{\text{zp}}E(\text{w}_{\text{Sn}}) + \Delta_{\text{zp}}E(\text{H}_3\text{O}^+) + \Delta V_{\text{w}}. \quad (8)$$

In Eqs. (7) and (8),  $\Delta_{\text{dp}}A(\text{H}_{\text{Br}}^+)$ ,  $\Delta_{\text{dp}}A(\text{w}_{\text{Sn}})$ , and  $\Delta_{\text{dp}}A(\text{H}_3\text{O}^+)$  are the deprotonation free energies of adsorbed proton, adsorbed water molecule, and aqueous hydronium cation, respectively.  $\Delta_{\text{dp}}A(\text{H}_{\text{Br}}^+)$  and  $\Delta_{\text{dp}}A(\text{w}_{\text{Sn}})$  are here calculated within the Marcus approximation:

$$\Delta_{\text{dp}}A(\text{H}_{\text{Br}}^+) = \frac{\langle \Delta_{\text{dp}}E(\text{H}_{\text{Br}}^+) \rangle_0 + \langle \Delta E(\text{H}_{\text{Br}}^+) \rangle_1}{2}, \quad (9)$$

$$\Delta_{\text{dp}}A(\text{w}_{\text{Sn}}) = \frac{\langle \Delta_{\text{dp}}E(\text{w}_{\text{Sn}}) \rangle_0 + \langle \Delta E(\text{w}_{\text{Sn}}) \rangle_1}{2}, \quad (10)$$

where  $\langle \Delta_{\text{dp}}E(\text{H}_{\text{Br}}^+) \rangle_0$  and  $\langle \Delta_{\text{dp}}E(\text{w}_{\text{Sn}}) \rangle_0$  are the average vertical energies of proton detachment, while  $\langle \Delta_{\text{dp}}E(\text{H}_{\text{Br}}^+) \rangle_1$  and  $\langle \Delta_{\text{dp}}E(\text{w}_{\text{Sn}}) \rangle_1$  the average vertical proton attachment. The former are calculated from a set of 200 configurations equally spaced in time. For each configuration, we vertically remove the acidic proton and recalculate the total-energy keeping the other atoms fixed. For the latter, we add a proton close to the surface Br site and to an adsorbed hydroxyl ion, respectively. Then, we perform structural relaxations in which all atoms except the inserted proton are fixed.  $\langle \Delta_{\text{dp}}E(\text{H}_{\text{Br}}^+) \rangle_1$

**Table 1**

List of the quantities (cf. text for definition) calculated to estimate free-energy differences, acidities, and band alignment reported in the main text. All values are given in eV.

Quantity	Value
$\Delta_{\text{dp}}A(\text{H}_3\text{O}^+)$	15.15 [102]
$\Delta_{\text{dp}}A(\text{H}_{\text{Br}}^+)$	15.40
$\Delta_{\text{dp}}A(\text{w}_{\text{Sn}})$	16.51
$\Delta_{\text{zp}}E(\text{H}_3\text{O}^+)$	0.32 [82]
$\Delta_{\text{zp}}E(\text{H}_{\text{Br}}^+)$	0.11
$\Delta_{\text{zp}}E(\text{w}_{\text{Sn}})$	0.30
$\Delta V_{\text{w}}$	−0.80
$\Delta V_{\text{sc}}$	1.40

and  $\langle \Delta_{\text{dp}}E(\text{w}_{\text{Sn}}) \rangle_1$  are hence computed from total-energy differences between the structural configurations with and without the proton. This procedure allows us to achieve converged results employing a set of 20 MD snapshots [32]. For  $\Delta_{\text{dp}}A(\text{H}_3\text{O}^+)$ , we employ the value calculated in Ref. [82].  $\Delta_{\text{zp}}E(\text{H}_{\text{Br}}^+)$ ,  $\Delta_{\text{zp}}E(\text{w}_{\text{Sn}})$ , and  $\Delta_{\text{zp}}E(\text{H}_3\text{O}^+)$  are the zero-point motion corrections accounting for the lack of nuclear quantum motions in our MD simulations. These contributions to the free energy are here calculated from the vibrational frequencies of the normal modes associated with the proton undergoing acidic dissociation [32,82]. Finally,  $\Delta V_{\text{w}}$  is the difference between the electrostatic potential of liquid water in the model of bulk water and in the respective bulk component of the interface model, which is required to align the calculations to an identical reference. This term is here calculated from the alignment of the O 2s of water molecules in the bulk liquid and those in the bulk-like region of the interface model [25,100]. We note that electrostatic finite-size effects for periodic charged supercell, which has been estimated with a correction scheme for the formation energy of charged defects at the interface [95,101], have been found here to be minimal, because of the strong screening of the semiconductor and the water molecules. Therefore, correction terms have been not included. All the calculated quantities are listed in Table 1.

We here estimate  $\text{p}K_a(\text{H}_{\text{Br}}^+) = -7.50$  and  $\text{p}K_a(\text{w}_{\text{Sn}}) = 7.75$ . Therefore, the surface Br site is a strong acid with protons being unlikely to be adsorbed on the perovskite surface under realistic pH conditions. At variance with this, the water molecule is found to increase its acidity when adsorbed on a surface Sn site from 15.74 to 7.75, slightly inferior to that previously reported for other tin-based semiconductors with a similar surface (i.e.  $\sim 5$  for SnO<sub>2</sub>). From the calculated values of  $\text{p}K_a$ , it follows that the dissociation reaction:



entails a free energy as large as 1.06 eV, again in accord with the low reactivity of this surface [76,78].

Next, we construct a logarithmic concentration diagram of adsorbed species from the calculated  $\text{p}K_a$ s, in analogy to those usually employed to visualize the concentration of weak acids in aqueous solution. To this end, we rearrange Eqs. (3) and (4) to explicit the pH-dependence of the adsorbed species:

$$\frac{[\text{Br}_{\text{surf}}]}{[\text{H}_{\text{Br}}^+]} = \frac{K_a(\text{H}_{\text{Br}}^+)}{[\text{H}_3\text{O}^+(\text{aq})]} = \frac{10^{-\text{p}K_a(\text{H}_{\text{Br}}^+)}}{10^{-\text{pH}}}, \quad (12)$$

$$\frac{[\text{OH}_{\text{Sn}}^-]}{[\text{w}_{\text{Sn}}]} = \frac{K_a(\text{w}_{\text{Sn}})}{[\text{H}_3\text{O}^+(\text{aq})]} = \frac{10^{-\text{p}K_a(\text{w}_{\text{Sn}})}}{10^{-\text{pH}}}, \quad (13)$$

and we impose:

$$c_{\text{Br}} = [\text{H}_{\text{Br}}^+] + [\text{Br}_{\text{surf}}], \quad (14)$$

$$c_{\text{Sn}} = \text{w}_{\text{Sn}} + [\text{OH}_{\text{Sn}}^-], \quad (15)$$

i.e. total concentration of an acidic species and of its the conjugated base is given by the surface site concentration (expressed in mol/dm<sup>2</sup>).

The concentration diagram for all the adsorbed species at the DMASnBr<sub>3</sub>(001)–water interface is presented in Fig. 2. We note that

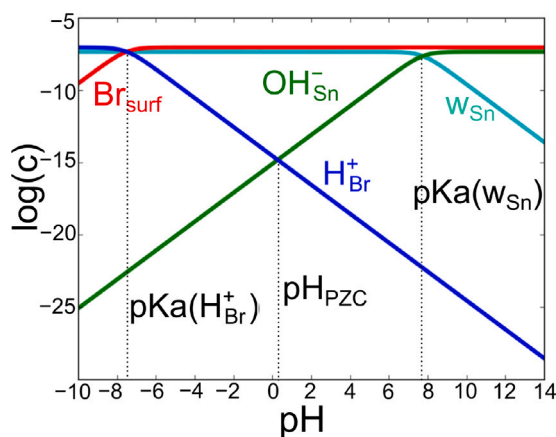


Fig. 2. pH-dependent diagram of surface coverage of at the DMASnBr<sub>3</sub>(001)–water interface. Concentrations are given in mol/dm<sup>2</sup>.

hydroxyl anions, initiating the water oxidation reaction within the faster alkaline mechanism, are abundant on the perovskite surface already in a mildly basic solution. In stark contrast, protons, the source of photoreduced hydrogen, are not likely to be found attached on the perovskite surface under the operative pH conditions of a heterogeneous photocatalytic system. We also pinpoint that the intersection between the pH-dependent concentrations of H<sub>Br</sub><sup>+</sup> and OH<sub>Sn</sub><sup>-</sup> define the pH at which the interface is charge-neutral, i.e. the so-called pH point of zero charge pH<sub>PZC</sub>. This is found to occur at 0.30, with concentration of ionic species being nevertheless negligible.

Since H adsorption on the surface is considered to be fundamental for the hydrogen evolution reaction on semiconductors [103,104], our results indicate the need of an alternative mechanism to justify the experimentally observed H<sub>2</sub> production. Therefore, we verify if the physical picture changes under photo-charging conditions, i.e. when photo-generated electrons are assimilated on the surface. In particular, we aim at verifying whether H adsorption on available surface Sn sites could be possible. To this end, we employ a simplified model in which the H defect is adsorbed on the bare DMASnBr<sub>3</sub>(001) surface, either on a surface Br or on a surface Sn atom. We consider three different charge states for the H defect: positive (+1), neutral (0), and (-1) negative, and for each of them, we relax the structures and calculate the total-energy difference  $\Delta E[H]^q$  (Cf. Supplementary Information for details of the calculations):

$$\Delta E[H]^q = E[H_{Sn}]^q - E[H_{Br}]^q, \quad (16)$$

where  $E[H_{Sn}]^q$  and  $E[H_{Br}]^q$  are the total energy of the slab bearing the H defect on surface Br and Sn, respectively.

From Fig. 3(a),  $\Delta E[H]^{+1} = 0.28$  eV indicates that a surface Sn is even more acidic than Br, in line with the cationic nature of the metal in MHPs. However, this is completely reversed when adding electrons to the system, as we compute for both  $\Delta E[H]^0$  and  $\Delta E[H]^{-1}$  negative values,  $-0.26$  and  $-1.03$  eV, respectively. We hence analyse the electronic densities of states (DOS) of the studied slabs at  $q = -1$ . The absence of any in-gap state for H<sub>Br</sub> [3(b)] means that the injected electrons are assimilated in the conduction band. In contrast, a localized state well below the conduction band appears in the DOS when H is adsorbed on a surface Sn site [3(c)]. Such a state is associated with charge localization on the Sn bearing the H and is extended up to the four neighbouring Br atoms, as highlighted by the projected density of state and illustrated from the isodensity plot of the highest occupied molecular orbital (HOMO) of the system [Fig. 3(c) and inset]. From the analysis of the centres of the maximally localized Wannier functions [105], which yield a real-space representation of the electron localization, we evince that an electron pair is actually on the adsorbed H (cf. Figure S2), i.e. a surface hydride has been formed.

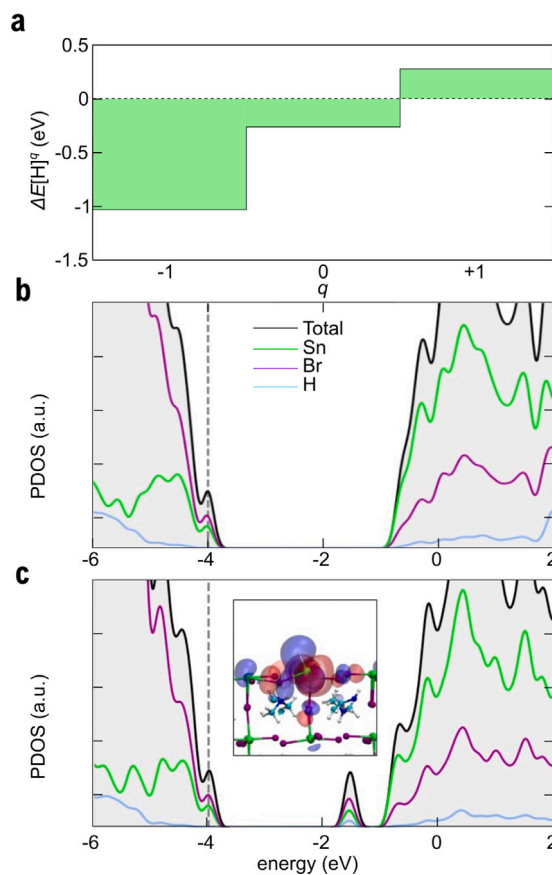
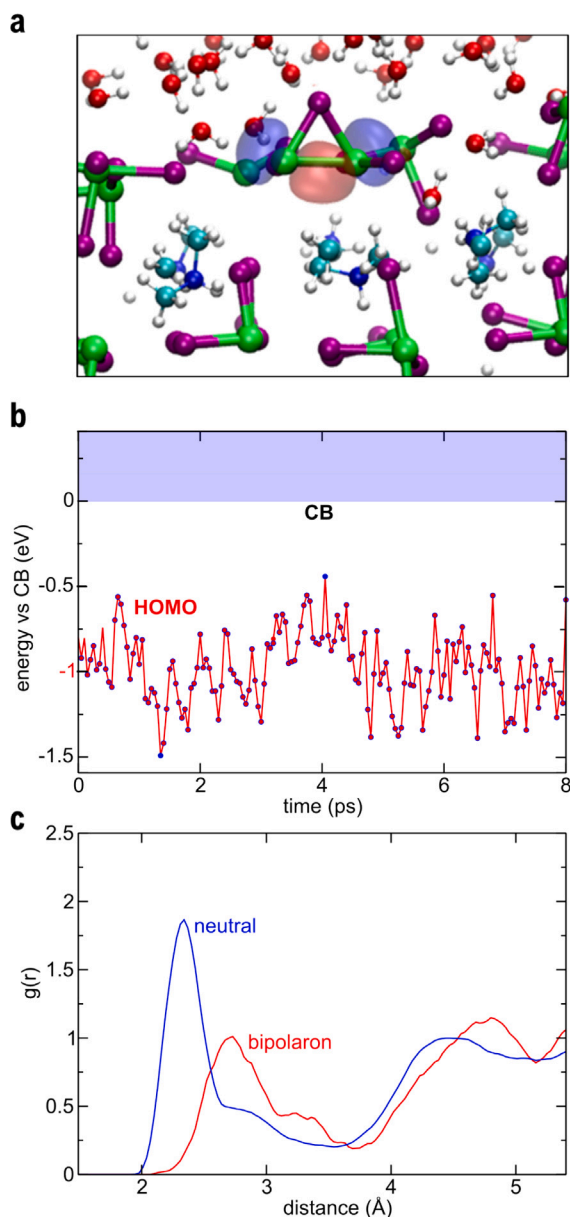


Fig. 3. (a)  $\Delta E[H]^q$  (cf. main text) for different values of  $q$ . Total and partial electronic density of states for the DMASnBr<sub>3</sub> (001) slab with a H defect in the charge state  $q = -1$  on (b) a surface Br and (c) a surface Sn (inset for the isodensity representation of the localized in-gap electronic state). The energy level of the highest occupied molecular orbital (HOMO) of the pristine neutral slab is indicated by a dashed vertical line.

The activity of surface sites should not change under photo-charging conditions if the photo-generated charges are delocalized/semilocalized [106]. As a matter of fact, we verify that the interface composition is barely affected when the MD simulation of the system is carried out with two extra electrons assimilated in the CB of the perovskite (cf. Figure S3). Therefore, in absence of any prior surface localization of electrons, hydride formation remains unlikely. However, the polaronic nature of charge carriers at the water–semiconductor interface can influence the acidity and reactivity of surface sites, e.g. TiO<sub>2</sub> [107,108], WO<sub>3</sub> [109], BiVO<sub>4</sub> [106,110–113], as well as the energy levels alignment [114]. On this subject, it has been recently demonstrated that electrons in THPs localize as small bipolarons, upon formation of a Sn–Sn bond with concomitant displacement of a lattice iodine [75]. Moreover, a reaction mechanism involving bipolaron formation has been recently proposed to justify the conspicuous photocatalytic activity of DMASnBr<sub>3</sub> [76].

In order to investigate the occurrence of such a localization mechanism at a realistic perovskite/water interface, we here construct a structural model in which we initially enforce the dimer formed by two surface tin atoms. Then, we carry out a 8-ps MD simulation of this system with two extra electrons. We observe that the dimeric structure, with an average bond length of 3.05 Å, and the associated electron localization [cf. Fig. 4(a)] are retained throughout the MD simulation, as evidenced by the time evolution of the energy of the highest occupied molecular orbital (HOMO) in Fig. 4(b) and of the bond length (cf. Figure S4). We also analyse how water molecules at



**Fig. 4.** (a) Isodensity representation and (b) time evolution of the HOMO for the electron bipolaron at the DMASnBr<sub>3</sub>/water interface. Shaded area for the conduction band. Energies are referred with respect to the CB edge of DMASnBr<sub>3</sub>. (c) Comparison between the Sn-O RDFs for tin atoms forming the dimer (solid line) and other tin atoms (dashed line) at the interface.

the interface interact with tin atoms forming the dimer. To this end, we compare the Sn-O RDF for the tin atoms belonging to the bipolaron with that achieved for the regular surface Sn atoms. The data, Fig. 4(c), reveal a noticeable change in the solvation of dimeric Sn atoms: the average Sn-O distance in the first solvation shell is increased from to 2.40 to ~2.80 Å as water molecules rearrange to point their hydrogen atoms towards the electron-rich moiety. This suggest a clear variation in the reactivity for the Sn atoms forming the dimer, which could be captured only with simulations explicitly including water molecules.

To further verify our reasoning, we place a single proton on top of a Sn atom forming the bipolaron and we let the system evolve via MD. We observe that the Sn-Sn is immediately broken while the adsorbed proton is reduced to a surface hydride with an average bond length

of 1.75 Å. Therefore, the bipolaron effectively acts as an “hotspot” for the otherwise implausible H adsorption. We also denote a substantial interaction between the negatively charged hydride and a surrounding water molecule pointing one of its hydrogen atoms towards it, with an average distance of ~1.80 Å (cf. Figure S5). This, combined with the poor alkalinity of neighbouring surface sites, suggests that the H<sub>2</sub> production may proceed via a Heyrovsky-like step [115], i.e. direct proton transfer from condensed-phase water molecule.

Finally, we refer the band edges of DMASnBr<sub>3</sub> to the energy levels of liquid water via a computational standard hydrogen electrode ( $\mu_{\text{SHE}}$ ) [82,116], defined by the reduction of the hydronium ion to gaseous hydrogen in aqueous solution [82,102], through the alignment of the plane-averaged electrostatic potential [24–26,100,117]. Our simulation of a water–semiconductor interface corresponding to  $\text{pH}_{\text{PZC}}$  allow us to define the position of the valence band edge at PZC [25]:

$$\epsilon_{\text{V}}^{\text{SHE}}(\text{PZC}) = \epsilon_{\text{V}}^{\text{theory}} - \mu_{\text{SHE}} - \Delta V_{\text{SC}} + \Delta V_{\text{w}}, \quad (17)$$

where  $\epsilon_{\text{V}}^{\text{theory}}$  is the calculated valence band edge of the bulk semiconductor,  $\Delta V_{\text{SC}} = V_{\text{SC}}(\text{bulk}) - V_{\text{SC}}(\text{int})$  the potential shift for the semiconductor at the interface, calculated from differences in the average electrostatic potentials in the bulk and at the interface. Analogously, the alignment of the conduction band edge is achieved as follows:

$$\epsilon_{\text{C}}^{\text{SHE}}(\text{PZC}) = \epsilon_{\text{V}}^{\text{SHE}} + E_{\text{g}}^{\text{theory}}, \quad (18)$$

i.e. by adding the calculated band gap to the valence band edge position. A schematic representation of the alignment scheme is provided in Supplementary Information, Figure S6. The band gap and band edges of DMASnBr<sub>3</sub> are taken from advanced electronic-structure calculations of Ref. [69],  $\mu_{\text{SHE}}$  from Ref. [102], while  $\Delta V_{\text{SC}}$  is computed in this study (cf. Table 1). We also include in the energy diagram (i) the H<sup>+</sup>/H<sub>2</sub> redox potential and (ii) the OH<sup>\*</sup>/H<sub>2</sub>O and OH<sup>\*</sup>/OH<sup>-</sup> reduction potentials, since dehydrogenation of the water molecule and oxidation of the hydroxyl ion represent the first step of the water oxidation reaction under acidic and alkaline conditions, respectively. In particular, for H<sup>+</sup>/H<sub>2</sub> and OH<sup>\*</sup>/OH<sup>-</sup>, we adopt the values calculated in the solution [82,102] while the OH<sup>\*</sup>/H<sub>2</sub>O redox level is inferred from a two-step process involving sequentially the deprotonation of the adsorbed molecule (calculated here) and the oxidation of the hydroxyl ion (from Ref. [82]). Finally, in order to adjust the band edges (aligned at  $\text{pH}_{\text{PZC}}$ ) and the standard redox levels (evaluated at pH = 0) to their values at pH = 7, we assume Nernstian behaviour for both, i.e. a shift of the levels towards the vacuum level with a rate of 0.059 eV per pH unit [25,27,32].

The calculated band alignment is reported in Fig. 5, with the VB (CB) edge of DMASnBr<sub>3</sub> being placed 1.25 (1.60) eV below (above) the SHE level, within 0.2 eV with that achieved in Ref. [69], in which explicit semiconductor–water interactions were not included, an additional evidence of the weak MHP–water interactions [78,118,119]. This implies that initiation of the water oxidation reaction via the acidic mechanism, involving dehydrogenation of a water molecule, is subject to a sizable energy barrier of 0.68 eV, since the redox level lies 1.93 eV above the SHE. However, we find that the OH<sup>-</sup>/OH<sup>\*</sup> level is almost resonant with the VB of the perovskite. This, in conjunction with the large fraction of hydroxyl anions adsorbed on the surface at pH > 7 [cf. Fig. 1(d)], points out that water oxidation should be more efficient in alkaline conditions, in accord with the experiment [69]. We note that, while most studies on MHPs have been dedicated to photocathodes, these findings suggest that exploring their possible application of as photoanodes might deserve a dedicated focus. The CB of DMASnBr<sub>3</sub> lies 1.17 eV above the H<sup>+</sup>/H<sub>2</sub> redox potential and such an alignment, while energetically favourable, is kinetically undesirable for charge transfer, as its rate features an inverse exponential dependence on the energy difference between initial and final states [120]. Furthermore, the extreme acidity of surface Br sites corresponds to negligible adsorption of protons in a large pH range, thus essentially ruling out a

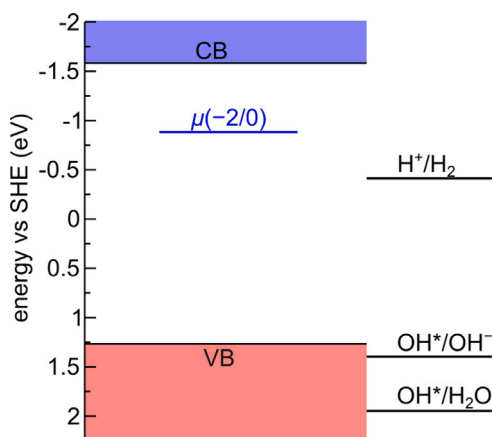


Fig. 5. VB and CB of DMASnBr<sub>3</sub> aligned with respect to the SHE at pH = 7. The alignment also includes the relevant water redox potentials and the  $\mu(-2/0)$  charge transition level associated with the electron bipolaron at the DMASnBr<sub>3</sub>/water interface (cf. main text).

traditional reaction mechanism. However, as small bipolarons occur at the interface, we need to evaluate also the related energy level.

To this end, we calculate the charge transition level associated with the electron bipolaron, which is defined as [106]:

$$\mu(-2/0) = \frac{G^{-2}[\text{bipol}] - G[\text{ref}]}{2} - \epsilon_V, \quad (19)$$

where  $G^{-2}[\text{bipol}]$  is the free energy of the bipolaron at the perovskite/water interface,  $G[\text{ref}]$  the free energy of the pristine interface model, and  $\epsilon_V$  the valence band edge of DMASnBr<sub>3</sub>. The free energy difference is again calculated as a thermodynamic integral of vertical energy gaps. In particular, within the Marcus approximation:

$$G^{-2}[\text{bipol}] - G[\text{ref}] = \frac{\langle \Delta E \rangle_0 + \langle \Delta E \rangle_1}{2}, \quad (20)$$

where  $\langle \Delta E \rangle_0$  corresponds to the energy of vertical injection of two electrons on the pristine systems, while  $\langle \Delta E \rangle_1$  to the energy of vertical removal of two electrons from the interface model bearing the bipolaron. Combining Eqs. (19) and (20), we obtain:

$$\mu(-2/0) = \frac{\langle \Delta E \rangle_0 + \langle \Delta E \rangle_1}{4} - \epsilon_V. \quad (21)$$

Consequently, the binding energy, referred with respect to the conduction band edge of the perovskite, is defined as:

$$E_b = \epsilon_C - \mu(-2/0). \quad (22)$$

We here estimate a binding energy of 0.70 eV, a value larger than those previously calculated for the bulk material (0.36 eV [75]) and the bare surface (up to 0.6 eV [76]). Such a result is in accord with the tendency, shown by liquid water, of stabilizing polaronic localization at the interface [106]. By placing  $\mu(-2/0)$  on the energy diagram of Fig. 5, we observe that the bipolaron energy level lies only 0.47 eV above the H<sup>+</sup>/H<sub>2</sub> redox level, which paves a more viable route towards hydrogen reduction, if compared to direct electron transfer from the CB of DMASnBr<sub>3</sub>. Therefore, our analysis highlights the clear role of electron bipolarons at the water–perovskite interface in promoting the photocatalytic H<sub>2</sub> production. However, it should be noted that, due to the robust stability of the bipolaron, the actual reaction mechanism may still involve steps generating an overpotential [76].

## 4. Conclusions

In conclusion, we performed first-principles MD simulations of the atomistic DMASnBr<sub>3</sub>–water interface, which, in conjunction with a grand-canonical formulation of adsorbates and defects, enabled a comprehensive description of the pH-dependent interface composition with particular focus on the negligible concentration of adsorbed protons within the pH range of an actual photocatalytic device. While such an inert surface chemistry would inhibit photocatalytic hydrogen production, our computational investigation of small electron bipolarons forming at the surface upon capture of photogenerated charges illustrated their dual beneficial role on photocatalysis. In fact, from one side, they provide the required charge localization for H adsorption in the form of surface hydride. On the other, the polaronic charge transition level was found to be favourably aligned with respect to the hydrogen reduction potential. The present results represent further proof that small polarons at the heterogeneous interface may be key to boost photocatalytic activity, sidestepping conventional reaction mechanisms.

## Associated content

Benchmark of the employed rVV10 functional vs. hybrid DFT, visual representation of the centres of Wannier functions for the hydride adsorbed on the DMASnBr<sub>3</sub>(001) surface, time evolution of the Sn–Sn bond length for the electron bipolaron, representative structural configuration of the hydride at the heterogeneous interface. Input files and snapshots of MD simulations are available at <https://github.com/fra85uni/dmasbr3-bipolaron>.

## CRedit authorship contribution statement

**Damiano Ricciarelli:** Writing – original draft, Investigation, Formal analysis, Visualization. **Edoardo Mosconi:** Software, Methodology, Investigation. **Julia Wiktor:** Conceptualization, Writing – review & editing, Methodology. **Lorenzo Malavasi:** Conceptualization, Writing – review & editing. **Francesco Ambrosio:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Investigation, Visualization. **Filippo De Angelis:** Supervision, Writing – review & editing, Resources, Funding acquisition, Conceptualization.

## 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.

## Acknowledgements

This work has been funded by the European Union project PERTPV under grant agreement no. 763977. F.D.A. acknowledges financial support from MIUR and Università degli Studi di Perugia through the program “Dipartimenti di Eccellenza 2018-2022” (Grant AMIS). F.D.A. also acknowledges funds by the European Union - NextGenerationEU under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041 - VITALITY. J. W. acknowledges funding from “Genie”, “Area of Advance - Materials Science” at Chalmers University of Technology, Sweden, and the Swedish Research Council (2019-03993). F.A. thankfully acknowledges the PRIN2022-PNRR project DELPHI (project code: P2022W9773).

## Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2024.01.268>.

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