

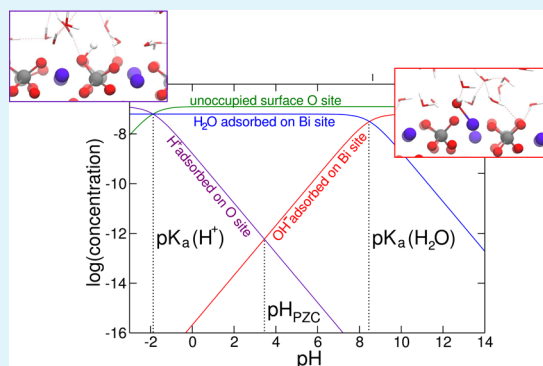
pH-Dependent Surface Chemistry from First Principles: Application to the $\text{BiVO}_4(010)$ –Water Interface

Francesco Ambrosio,^{*} Julia Wiktor,[†] and Alfredo Pasquarello[‡]

Chaire de Simulation à l'Echelle Atomique (CSEA), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

ABSTRACT: We present a theoretical formulation for studying the pH-dependent interfacial coverage of semiconductor–water interfaces through ab initio electronic structure calculations, molecular dynamics simulations, and the thermodynamic integration method. This general methodology allows one to calculate the acidity of the individual adsorption sites on the surface and consequently the pH at the point of zero charge, pH_{PZC} , and the preferential adsorption mode of water molecules, either molecular or dissociative, at the semiconductor–water interface. The proposed method is applied to study the $\text{BiVO}_4(010)$ –water interface, yields a pH_{PZC} in excellent agreement with the experimental characterization. Furthermore, from the calculated pK_a values of the individual adsorption sites, we construct an ab initio concentration diagram of all adsorbed species at the interface as a function of the pH of the aqueous solution. The diagram clearly illustrates the pH-dependent coverage of the surface and indicates that protons are found to be significantly adsorbed ($\sim 1\%$ of available sites) only in highly acidic conditions. The surface is found to be mostly covered by molecularly adsorbed water molecules in a wide interval of pH values ranging from 2 to 8. Hydroxyl ions are identified as the dominant adsorbed species at pH larger than 8.2.

KEYWORDS: semiconductor–water interface, pH-dependent interfacial coverage, ab initio MD simulation



1. INTRODUCTION

Photocatalytic water splitting is a natural process occurring in photosynthesis. In the last decades, large efforts have been devoted to mimic nature through artificial photocatalysis at the semiconductor–water interface.^{1–6} In this context, the search for the ideal photocatalyst has been the major objective of the scientific community.^{7–12} In fact, photocatalysts are instrumental in determining the efficiency of redox processes at aqueous interfaces. However, experiments are unable to efficiently screen materials providing efficient water splitting. Preliminary ab initio screenings of candidate materials are based either on their electronic properties, that is, band gap and band edges^{7–9,11–13} or on the overpotentials associated with the multistep water oxidation reaction.¹⁴ However, simplified computational protocols, that is, lack of explicit solvents, use of 0 K structural models, and inaccurate density functionals, are likely to miss important physical aspects, thus affecting and possibly invalidating these screening procedures.

In fact, a main issue in the theoretical description of physical processes occurring at solid–liquid interfaces arises from the complex nature of such interfaces, which often eludes even the experimental characterization. In the case of semiconductor–water systems, the nature of the heterogeneous interface depends upon multiple factors, such as the pH of the aqueous solution, the structural and electronic properties of the surface, the possible presence of surface defects, the electrolyte, and

additives in the aqueous solution. The individual and combined effects of each of these factors are difficult to discern with experiments, and the simultaneous inclusion of all of these variables in a single simulation is possibly beyond reach.

Even if one considers the simplest case, that is, a defect-free solid surface immersed in an aqueous environment where only water molecules, protons, and hydroxyl ions can be adsorbed, the nature of the heterogeneous interface is still not obvious. First, it depends on the structural and electronic properties of the surface, which may favor either molecular adsorption of water molecules or their spontaneous dissociation on the exposed adsorption sites. Furthermore, the coverage of the interface is pH-dependent: adsorption of protons is favored in acidic conditions and that of hydroxyl ions in basic conditions, thus implying the development of either a positive or a negative surface charge at the interface, respectively. It is actually possible to measure the pH at the point of zero charge for a given surface, defined as the pH value for which no surface charge is observed, that is, for which the concentration of adsorbed protons is equal to that of adsorbed hydroxyl ions. This is done through simple acid–base titration and photoelectrochemical measurements. However, experiments are

Received: October 31, 2017

Accepted: March 2, 2018

Published: March 2, 2018

typically unable to characterize the underlying acidities of the individual adsorption sites and hence cannot provide detailed information about the structural and electronic properties of the interface. Moreover, recent molecular dynamics (MD) simulations of semiconductor–water interfaces have proved not to be always sufficient to discern between molecular and dissociative adsorption of water molecules on the semiconductor surface.¹³ Therefore, an analysis of the structural properties at semiconductor–water interfaces based on direct simulations is sometimes not actually feasible. Nevertheless, this piece of information is instrumental to understand the mechanism of heterogeneous water splitting. For instance, BiVO₄, one of the most promising materials for water splitting,^{15–18} has its intrinsic photocatalytic properties far from being understood.^{18–23} In particular, recent measurements indicate, contrary to previous assumptions that the efficiency of water splitting on this semiconductor is rather promising, even without the deposition of a catalyst on the surface.²³

Semiempirical surface protonation models have emerged in the last decades as practical tools for the determination of intrinsic acidities of surface sites.^{24–30} These models usually express the acidic constant K_a of a given surface as a function of the bond valence of the involved atom, while including other effects (i.e., solvation and hydrogen bonding) with implicit models.^{24–30} However, the accuracy of some of these approximations has been questioned.^{28–31} More recently, the evaluation of acidities of adsorption sites at the semiconductor–water interface from MD simulations has been proposed.³¹ However, although specific computational protocols have been set up, current theoretical formulations do not include organically the multiple factors influencing the coverage of the interface and are hence limited to a few cases.^{31–33} In this framework, a comprehensive theoretical formulation allowing for an in-depth analysis of semiconductor–water interfaces is highly desirable.

We here present a general formulation to study the pH-dependent interfacial coverage of semiconductor–water interfaces based on a grand-canonical formulation for solutes in an aqueous solution and species adsorbed on the surface. The proposed theoretical framework combined with specific computational protocols based on ab initio MD simulations allows us to accurately calculate the pH at the point of zero charge, pH_{PZC} , for a generic surface and the acidity of its various adsorption sites. This method is applied to the study of the interface between water and BiVO₄. By modeling the adsorption of H₂O, H⁺, and OH[−] at the BiVO₄(010)–water interface, we yield a pH_{PZC} in excellent agreement with the experiment and are able to characterize the acid–base properties of the surface in connection with the surface reconstructions induced by the adsorption of charged solutes. Furthermore, we present an ab initio concentration diagram of all species at the interface as a function of the pH of the aqueous solution. The implications of our results on the mechanism of the water oxidation reaction at the BiVO₄(010) surface are discussed.

This paper is organized as follows. In section 2, we present the theoretical formulation developed to calculate the pH at the point of zero charge for a semiconductor at the interface with liquid water. In section 3, we report on the details of the MD simulations and discuss the structural properties of the interfaces. In section 4, we describe the acid–base properties of BiVO₄(010) in an aqueous environment and discuss the

calculated pH_{PZC} and the $\text{p}K_a$ of the surface adsorption sites. The conclusions are drawn in section 5.

2. THEORY

2.1. Grand-Canonical Formulation for Solutes in an Aqueous Solution. The formation Gibbs free energy of a solute X in a charge state q is given by³⁴

$$G_{\text{f}}^q[\text{X}] = G^q[\text{X}] - G[\text{bulk}] - \sum_i n_i \mu_i + q(\epsilon_{\text{v-w}} + \mu_{\text{e}}) + E_{\text{corr}}^q \quad (1)$$

where $G^q[\text{X}]$ is the Gibbs free energy of the solute X in the charged state q , $G[\text{bulk}]$ is the Gibbs free energy of bulk water, μ_i is the chemical potential of the added/subtracted species i , n_i is the number of added/subtracted i atoms, $\epsilon_{\text{v-w}}$ is the valence band edge of bulk liquid water, μ_{e} is the electron chemical potential, and E_{corr}^q is a correction term taking into account electrostatic finite-size effects. In this work, the Freysoldt–Neugebauer–Van de Walle scheme^{35,36} is employed to correct the total energies achieved with calculations of periodic charged supercells. In ref 34, it has been shown that, when applied to charged solutes (H₃O⁺ and OH[−]) in a periodic supercell containing 64 water molecules, corrections to total energies are as small as 0.03 eV because of the high dielectric constant of liquid water at ambient conditions (78.3). In this formulation, the redox level $\mu_{\text{e}}(q/q')$ is defined as the electron chemical potential for which the free energies of formation of a solute X in the charge states q and q' are equal, $\Delta G(q/q') = 0$.^{36,37} For the aqueous solutions considered in this work, the volume changes lead to negligible contributions to the Gibbs free energy. Therefore, these volume effects are here neglected and we effectively consider the Helmholtz free energy.

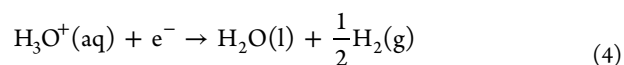
The thermodynamic integration method is used to calculate free-energy differences. In this technique, an auxiliary Hamiltonian is defined as a linear combination of the Hamiltonians of the reactant and the product:^{38,39}

$$\mathcal{H}_{\eta} = (1 - \eta)\mathcal{H}_{\text{R}} + \eta\mathcal{H}_{\text{P}} \quad (2)$$

where $0 < \eta < 1$ is the Kirkwood coupling parameter.^{38,39} For each value of η , the time-averaged vertical energy difference between the reactant and the product $\langle \Delta E \rangle_{\eta}$ is calculated. The free-energy change of the reaction ΔA is given by the integration of the $\langle \Delta E \rangle_{\eta}$ calculated at varying η

$$\begin{aligned} \Delta A &= A(\text{P}) - A(\text{R}) = A(\eta = 1) - A(\eta = 0) \\ &= \int_0^1 \langle \Delta E \rangle_{\eta} d\eta \end{aligned} \quad (3)$$

Within the present formulation, we define a computational standard hydrogen electrode (SHE)^{34,40} based on the reduction of the aqueous hydronium ion



The respective redox level is given by the following expression³⁴

$$\mu_{\text{SHE}} = G[\text{bulk}] - G[\text{H}_3\text{O}^+(\text{aq})] - \epsilon_{\text{v-w}} + \mu_{\text{H}} - E_{\text{corr}}^{+1} \quad (5)$$

where

$$G[\text{bulk}] - G[\text{H}_3\text{O}^+(\text{aq})] = \int_0^1 \langle \Delta_{\text{dp}} E_{\text{H}_3\text{O}^+}(\text{aq}) \rangle_\eta d\eta - \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+} \\ = \Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} - \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+} \quad (6)$$

$\Delta_{\text{dp}} A_{\text{H}_3\text{O}^+}$ is the integral associated with the deprotonation reaction of the hydronium cation, $\Delta_{\text{zp}} E_{\text{H}_3\text{O}^+}$ is a correction that accounts for the lack of nuclear quantum motions in our MD simulations, and μ_{H} is the chemical potential of hydrogen. The SHE level has previously been aligned with respect to the band edges of liquid water for the functional adopted in this work.^{34,41}

2.2. Definition of pH. We here define the pH within our formulation and demonstrate its connection with the proton chemical potential μ_{H^+} . The concentration of hydronium ions in solution $c_{\text{H}^+}(\text{aq})$ and hence the pH can be expressed from the respective formation energy^{34,42}

$$c_{\text{H}^+}(\text{aq}) = c_0 e^{-G_{\text{f}}[\text{H}_3\text{O}^+(\text{aq})]/k_{\text{B}}T} = 10^{-\text{pH}} \quad (7)$$

where c_0 is the number of water moles in 1 L of liquid water (55.5 mol/L), T is the temperature, and k_{B} is the Boltzmann constant. Isolating $G_{\text{f}}[\text{H}_3\text{O}^+(\text{aq})]$ in eq 7, we obtain the following expression

$$G_{\text{f}}[\text{H}_3\text{O}^+(\text{aq})] = k_{\text{B}}T(\ln c_0 + \ln 10 \cdot \text{pH}) \quad (8)$$

From eqs 1 and 6, $G_{\text{f}}[\text{H}_3\text{O}^+(\text{aq})]$ also reads as follows

$$G_{\text{f}}[\text{H}_3\text{O}^+(\text{aq})] = -\Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} + \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+} - \mu_{\text{H}} + \mu_{\text{e}} \\ + \epsilon_{\text{v-w}} + E_{\text{corr}}^+ \quad (9)$$

Therefore, we combine eqs 8 and 9 and isolate μ_{e}

$$\mu_{\text{e}} = \Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} - \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+} + \mu_{\text{H}} - \epsilon_{\text{v-w}} - E_{\text{corr}}^+ \\ + k_{\text{B}}T(\ln c_0 + \ln 10 \cdot \text{pH}) \quad (10)$$

It should be noted that the chemical potentials of the hydrogen atom, the proton, and the electron are related through the following expression⁴²

$$\mu_{\text{H}} = \mu_{\text{e}} + \mu_{\text{H}^+} \quad (11)$$

By substituting eq 11 into eq 10, we obtain the following expression

$$\mu_{\text{H}^+} = -\Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} + \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+} + \epsilon_{\text{v-w}} + E_{\text{corr}}^+ \\ - k_{\text{B}}T(\ln c_0 + \ln 10 \cdot \text{pH}) \quad (12)$$

which illustrates the direct connection between the chemical potential of the isolated proton with the pH of the solution.

2.3. Point of Zero Charge of Surfaces in an Aqueous Environment. The pH at the point of zero charge for a solid surface at the interface with liquid water is defined as the pH for which the concentration of adsorbed protons, $c_{\text{H}^+}(\text{ads})$, is equal to that of adsorbed hydroxyl ions, $c_{\text{OH}^-}(\text{ads})$

$$c_{\text{H}^+}(\text{ads}) = c_{\text{OH}^-}(\text{ads}) \quad (13)$$

$c_{\text{H}^+}(\text{ads})$ and $c_{\text{OH}^-}(\text{ads})$ can be expressed, in analogy to the definition of defect concentrations in crystalline materials, in terms of the formation energies of the proton and of the hydroxyl ion on a given surface

$$c_{\text{H}^+}(\text{ads}) = \sum_{i=1}^N c_{\text{H}^+}(i) = \sum_{i=1}^N c_i e^{-G_{\text{f}}[\text{H}^+]_i/k_{\text{B}}T} \quad (14)$$

and

$$c_{\text{OH}^-}(\text{ads}) = \sum_{i=1}^N c_{\text{OH}^-}(i) = \sum_{i=1}^N c_i e^{-G_{\text{f}}[\text{OH}^-]_i/k_{\text{B}}T} \quad (15)$$

where the sum runs over the number N of nonequivalent adsorption sites at the surface, c_i is the surface concentration of the adsorption site i , and $G_{\text{f}}[\text{H}^+]_i$ and $G_{\text{f}}[\text{OH}^-]_i$ are the formation energies of the proton and the hydroxyl ion at the i -th adsorption site, respectively. Equations 14 and 15 account for all possible sites at the semiconductor–water interface, including defects and geometrically different sites.

The formulation is largely simplified by considering an ideal M_xA_y surface, where M is a metal site and A is a nonmetal site. We also assume that all M and A sites are equivalent and that H^+ is adsorbed only on the A sites, whereas OH^- is adsorbed only at M sites. In fact, the cationic metal is likely to strongly prefer the adsorption of the negatively charged hydroxyl. Analogously, adsorption of H^+ is preferred on the anionic site. These assumptions are equivalent to the following inequalities

$$G_{\text{f}}[\text{H}^+]_{\text{M}} \gg G_{\text{f}}[\text{OH}^-]_{\text{M}} \quad (16)$$

and

$$G_{\text{f}}[\text{OH}^-]_{\text{A}} \gg G_{\text{f}}[\text{H}^+]_{\text{A}} \quad (17)$$

where $G_{\text{f}}[\text{H}^+]_{\text{M}}$, $G_{\text{f}}[\text{OH}^-]_{\text{M}}$, $G_{\text{f}}[\text{H}^+]_{\text{A}}$, and $G_{\text{f}}[\text{OH}^-]_{\text{A}}$ are the formation energies of H^+ and OH^- adsorbed on the M and A sites, respectively. Hence, eqs 14 and 15 are reformulated as follows

$$c_{\text{H}^+}(\text{ads}) = c_{\text{A}} e^{-G_{\text{f}}[\text{H}^+]_{\text{A}}/k_{\text{B}}T} \quad (18)$$

and

$$c_{\text{OH}^-}(\text{ads}) = c_{\text{M}} e^{-G_{\text{f}}[\text{OH}^-]_{\text{M}}/k_{\text{B}}T} \quad (19)$$

At the pH of zero-point charge [cf. eq 13]

$$c_{\text{A}} e^{-G_{\text{f}}[\text{H}^+]_{\text{A}}/k_{\text{B}}T} = c_{\text{M}} e^{-G_{\text{f}}[\text{OH}^-]_{\text{M}}/k_{\text{B}}T} \quad (20)$$

$G_{\text{f}}[\text{H}^+]_{\text{A}}$ and $G_{\text{f}}[\text{OH}^-]_{\text{M}}$ can also be expressed using a grand-canonical formulation for adsorbates at the semiconductor–water interface, which is again equivalent to that used for defects in crystalline materials and solutes in an aqueous solution. We hence define the Gibbs free energy of formation of an adsorbate Y in the charged state q , as follows

$$G_{\text{f}}^q[\text{Y}] = G^q[\text{Y}] - G[\text{ref}] - \sum_i n_i \mu_i + q[\epsilon_{\text{v-w}}(\text{int}) + \mu_{\text{e}}] \\ + E_{\text{corr}}^q(\text{int}) \quad (21)$$

where $G^q[\text{Y}]$ is the Gibbs free energy of the adsorbate Y in the charged state q , $G[\text{ref}]$ is the Gibbs free energy of the reference interface system, μ_i is the chemical potential of the added/subtracted species i , n_i is the number of added/subtracted atoms of the i -th atomic species (positive for added species, negative for subtracted species), $\epsilon_{\text{v-w}}(\text{int})$ is the valence band edge of liquid water at the interface with the semiconductor, μ_{e} is the electron chemical potential, and $E_{\text{corr}}^q(\text{int})$ is a correction term taking into account electrostatic finite-size effects induced by the presence of a charge close to the interface between two materials. This term is calculated in this work using the

correction scheme for the formation energy of charged defects at the interface, introduced in ref 43 for surfaces and interfaces. Because of the high dielectric constants of both BiVO₄ and liquid water, the calculated correction terms are rather small (below 0.02 eV) for the charged species considered in this work (H⁺ and OH[−]). In our formulation, $G[\text{ref}]$ is the neutral semiconductor–water interface at equilibrium, as achieved from MD simulations. $\epsilon_{v-w}(\text{int})$ can be related to ϵ_{v-w} through

$$\epsilon_{v-w}(\text{int}) = \epsilon_{v-w} - \Delta V_w \quad (22)$$

where

$$\Delta V_w = V_w(\text{bulk}) - V_w(\text{int}) \quad (23)$$

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 (cf. Figure 1). Substituting in eq 21, we obtain

$$G_f^q[Y] = G^q[Y] - G[\text{ref}] - \sum_i n_i \mu_i + q[\epsilon_{v-w} - \Delta V_w + \mu_e] + E_{\text{corr}}^q(\text{int}) \quad (24)$$

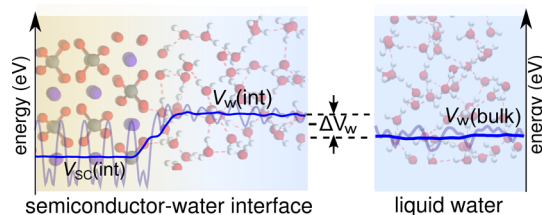


Figure 1. Schematic representation of the alignment scheme. The lineup between the average electrostatic potential in bulk liquid water $V_w(\text{bulk})$ and at the semiconductor–water interface $V_w(\text{int})$ is achieved through ΔV_w [cf. eq 23].

The formation free energies of adsorbed H⁺ and OH[−] read as follows

$$G_f[\text{H}^+]_A = G[\text{H}^+]_A - G[\text{ref}] - \mu_H + \epsilon_{v-w} - \Delta V_w + \mu_e + E_{\text{corr}}^+(\text{int}) \quad (25)$$

and

$$G_f[\text{OH}^-]_M = G[\text{OH}^-]_M - G[\text{ref}] + \mu_H - \epsilon_{v-w} + \Delta V_w - \mu_e + E_{\text{corr}}^-(\text{int}) \quad (26)$$

The free-energy differences appearing in eqs 25 and 26 read as follows

$$\begin{aligned} G[\text{H}^+]_A - G[\text{ref}] &= - \int_0^1 \langle \Delta_{\text{dp}} E_{\text{H}_A^+} \rangle_\eta d\eta + \Delta_{\text{zp}} E_{\text{H}_A^+} \\ &= -\Delta_{\text{dp}} A_{\text{H}_A^+} + \Delta_{\text{zp}} E_{\text{H}_A^+} \end{aligned} \quad (27)$$

and

$$\begin{aligned} G[\text{OH}^-]_M - G[\text{ref}] &= \int_0^1 \langle \Delta_{\text{dp}} E_{\text{w}_M} \rangle_\eta d\eta - \Delta_{\text{zp}} E_{\text{w}_M} \\ &= \Delta_{\text{dp}} A_{\text{w}_M} - \Delta_{\text{zp}} E_{\text{w}_M} \end{aligned} \quad (28)$$

where $\Delta_{\text{dp}} A_{\text{H}_A^+}$ and $\Delta_{\text{dp}} A_{\text{w}_M}$ are the integrals associated with the deprotonation reaction of a proton adsorbed on a surface site A and of a water molecule adsorbed on a surface site M, respectively. $\Delta_{\text{zp}} E_{\text{H}_A^+}$ and $\Delta_{\text{zp}} E_{\text{w}_M}$ are the zero-point motions of a proton adsorbed on a surface site A and of a proton belonging to a water molecule adsorbed on a site M, respectively. Equation 20 can be reformulated as follows

$$G_f[\text{OH}^-] - G_f[\text{H}^+] = k_B T \ln \left(\frac{c_M}{c_A} \right) \quad (29)$$

Substituting eqs 25–28 into eq 29 and isolating the electron chemical potential μ_e , we obtain the following expression

$$\begin{aligned} 2\mu_e &= \Delta_{\text{dp}} A_{\text{w}_M} + \Delta_{\text{dp}} A_{\text{H}_A^+} + 2\mu_H - \Delta_{\text{zp}} E_{\text{w}_M} - \Delta_{\text{zp}} E_{\text{H}_A^+} \\ &\quad - 2\epsilon_{v-w} + 2\Delta V_w + E_{\text{corr}}^-(\text{int}) - E_{\text{corr}}^+(\text{int}) - k_B T \ln \left(\frac{c_M}{c_A} \right) \end{aligned} \quad (30)$$

We hence replace μ_e with the definition provided in eq 10, thus effectively achieving an expression for pH_{PZC}

$$\begin{aligned} \text{pH}_{\text{PZC}} &= \frac{\Delta_{\text{dp}} A_{\text{w}_M} + \Delta_{\text{dp}} A_{\text{H}_A^+} - 2\Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} + 2\Delta V_w}{2 k_B T \ln 10} \\ &\quad + \frac{-\Delta_{\text{zp}} E_{\text{w}_M} - \Delta_{\text{zp}} E_{\text{H}_A^+} + 2\Delta_{\text{zp}} E_{\text{H}_3\text{O}^+}}{2 k_B T \ln 10} \\ &\quad + \frac{E_{\text{corr}}^-(\text{int}) - E_{\text{corr}}^+(\text{int}) + 2E_{\text{corr}}^+}{2 k_B T \ln 10} \\ &\quad - \frac{1}{2} \left[\log \left(\frac{c_M}{c_A} \right) \right] - \log c_0 \end{aligned} \quad (31)$$

2.4. Acidity of Molecules at the Adsorption Site.

Calculated values of pH_{PZC} allow for a straightforward comparison with the experiment, which, however, is generally unable of measuring the individual acidities of adsorbed molecules at each surface site. Our formulation allows us to consistently calculate the acid dissociation constant for each molecule capable of donating or accepting protons at each adsorption site. Let us consider the adsorption of the generic acid HB on the i -th adsorption site of a given surface. This undergoes the following acid–base equilibrium



The respective K_a reads as follows

$$K_a(\text{HB}_i) = \frac{[\text{H}^+(\text{aq})][\text{B}_i^-]}{[\text{HB}_i]} \quad (33)$$

For $\text{pH} = \text{p}K_a(\text{HB}_i)$, the concentration of the adsorbed HB and that of the adsorbed conjugated base B[−] are equal: $c_{\text{HB}_i} = c_{\text{B}_i^-}$. Each concentration is again related to the formation free energy of the respective adsorbed species

$$c_{\text{HB}_i} = c_i e^{G_f[\text{HB}_i]/k_B T} \quad (34)$$

and

$$c_{\text{B}_i^-} = c_i e^{G_f[\text{B}_i^-]/k_B T} \quad (35)$$

The formation free energies of adsorbed HB and B[−] read as follows

$$G_f[\text{HB}]_i = G[\text{HB}]_i - G[\text{ref}] - \mu_{\text{H}} - \mu_{\text{B}} \quad (36)$$

and

$$G_f[\text{B}^-]_i = G[\text{B}^-]_i - G[\text{ref}] - \mu_{\text{B}} - \epsilon_{\text{v-w}} + \Delta V_{\text{w}} - \mu_{\text{e}} + E_{\text{corr}}^{-1}(\text{int}) \quad (37)$$

From eqs 34–37, μ_{e} reads as follows

$$\mu_{\text{e}} = G[\text{B}^-]_i - G[\text{HB}]_i + \mu_{\text{H}} - \epsilon_{\text{v-w}} + \Delta V_{\text{w}} + E_{\text{corr}}^{-1}(\text{int}) \quad (38)$$

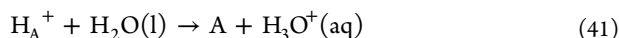
where

$$\begin{aligned} G[\text{B}^-]_i - G[\text{HB}]_i &= \int_0^1 \langle \Delta_{\text{dp}} E_{\text{HB}_i} \rangle_{\eta} d\eta - \Delta_{\text{zp}} E_{\text{HB}_i} \\ &= \Delta_{\text{dp}} A_{\text{HB}_i} - \Delta_{\text{zp}} E_{\text{HB}_i} \end{aligned} \quad (39)$$

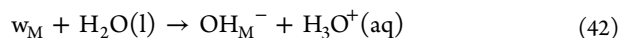
is the thermodynamic integral associated with the deprotonation of the adsorbed HB molecule. By replacing μ_{e} with eq 10, we obtain $\text{p}K_{\text{a}}(\text{HB}_i)$

$$\begin{aligned} \text{p}K_{\text{a}}(\text{HB}_i) &= \frac{\Delta_{\text{dp}} A_{\text{HB}_i} - \Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} + \Delta V_{\text{w}}}{\ln 10 k_{\text{B}} T} \\ &+ \frac{-\Delta_{\text{zp}} E_{\text{HB}_i} + \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+}}{\ln 10 k_{\text{B}} T} \\ &+ \frac{E_{\text{corr}}^{-1}(\text{int}) + E_{\text{corr}}^{+1}}{\ln 10 k_{\text{B}} T} - \log c_0 \end{aligned} \quad (40)$$

We apply our formulation to the simple cases of H⁺ adsorbed on the anionic site A of a semiconductor surface and to OH[−] adsorbed on the cationic site M. These solutes are subject to the following acid–base equilibria



and



We apply eq 40 to both cases, thus achieving the following expressions for the $\text{p}K_{\text{a}}$ of H⁺ adsorbed on A and of OH[−] adsorbed on M, respectively

$$\begin{aligned} \text{p}K_{\text{a}}(\text{H}_A^+) &= \frac{\Delta_{\text{dp}} A_{\text{H}_A^+} - \Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} + \Delta V_{\text{w}}}{k_{\text{B}} T \ln 10} \\ &+ \frac{-\Delta_{\text{zp}} E_{\text{H}_A^+} + \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+}}{k_{\text{B}} T \ln 10} \\ &+ \frac{-E_{\text{corr}}^{+1}(\text{int}) + E_{\text{corr}}^{-1}}{k_{\text{B}} T \ln 10} - \log c_0 \end{aligned} \quad (43)$$

and

$$\begin{aligned} \text{p}K_{\text{a}}(\text{w}_M) &= \frac{\Delta_{\text{dp}} A_{\text{w}_M} - \Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} + \Delta V_{\text{w}}}{k_{\text{B}} T \ln 10} \\ &+ \frac{-\Delta_{\text{zp}} E_{\text{w}_M} - \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+}}{k_{\text{B}} T \ln 10} \\ &+ \frac{+E_{\text{corr}}^{-1}(\text{int}) + E_{\text{corr}}^{+1}}{k_{\text{B}} T \ln 10} - \log c_0 \end{aligned} \quad (44)$$

From eqs 31, 43, and 44, pH_{PZC} reads as follows

$$\text{pH}_{\text{PZC}} = \frac{\text{p}K_{\text{a}}(\text{H}_A^+) + \text{p}K_{\text{a}}(\text{w}_M)}{2} - \frac{1}{2} \left[\log \left(\frac{c_{\text{M}}}{c_{\text{A}}} \right) \right] \quad (45)$$

2.5. Dissociation Constant of Adsorbed Water Molecules. The relative stability of molecularly and dissociatively adsorbed water molecules can be derived from the calculated $\text{p}K_{\text{a}}$ values. Let us consider the following dissociation reaction



for which the dissociation constant reads as follows

$$K_{\text{d}}(\text{w}_M) = \frac{[\text{OH}_M^-][\text{H}_A^+]}{[\text{w}_M][\text{A}]} \quad (47)$$

Again, from the relationship between concentration and formation free energy, we obtain

$$K_{\text{d}}(\text{w}_M) = e^{-(G_{\text{f}}[\text{OH}^-]_{\text{M}} + G_{\text{f}}[\text{H}^+]_{\text{A}} - G_{\text{f}}[\text{w}_M] - G_{\text{f}}[\text{A}]) / k_{\text{B}} T} \quad (48)$$

where $G_{\text{f}}[\text{w}_M]$ and $G_{\text{f}}[\text{A}]$ are the formation free energies of the adsorbed water molecule on an M site and of a free A site, respectively. Defining the free energy of dissociation of an adsorbed water molecule

$$\Delta A_{\text{d}}(\text{w}_M) = G_{\text{f}}[\text{OH}^-]_{\text{M}} + G_{\text{f}}[\text{H}^+]_{\text{A}} - G_{\text{f}}[\text{w}_M] - G_{\text{f}}[\text{A}] \quad (49)$$

we then obtain from eq 48

$$K_{\text{d}}(\text{w}_M) = e^{-\Delta A_{\text{d}}(\text{w}_M) / k_{\text{B}} T} \quad (50)$$

and

$$\Delta A_{\text{d}}(\text{w}_M) = -k_{\text{B}} T \ln K_{\text{d}}(\text{w}_M) = -k_{\text{B}} T \ln 10 \cdot \log K_{\text{d}}(\text{w}_M) \quad (51)$$

From eqs 41 and 42, we have

$$K_{\text{a}}(\text{H}_A^+) = \frac{[\text{A}][\text{H}_3\text{O}^+(\text{aq})]}{[\text{H}_A^+]} \quad (52)$$

and

$$K_{\text{a}}(\text{w}_M) = \frac{[\text{OH}_M^-][\text{H}_3\text{O}^+(\text{aq})]}{[\text{w}_M]} \quad (53)$$

From eqs 47, 52, and 53, we can express $K_{\text{d}}(\text{w}_M)$ from $K_{\text{a}}(\text{H}_A^+)$ and $K_{\text{a}}(\text{w}_M)$

$$K_{\text{d}}(\text{w}_M) = \frac{K_{\text{a}}(\text{w}_M)}{K_{\text{a}}(\text{H}_A^+)} \quad (54)$$

Therefore, from eqs 51 and 54, the free energy of dissociation of an adsorbed water molecule reads as follows:

$$\Delta A_{\text{d}}(\text{w}_M) = \ln 10 \cdot k_{\text{B}} T [\text{p}K_{\text{a}}(\text{w}_M) - \text{p}K_{\text{a}}(\text{H}_A^+)] \quad (55)$$

3. MD SIMULATIONS OF $\text{BiVO}_4(010)$ –WATER INTERFACES

We model the neutral $\text{BiVO}_4(010)$ –water interface with an orthorhombic supercell ($a = 10.39$, $b = 10.18$, and $c = 36.17$ Å, cf. Figure 2a) containing 56 H_2O molecules and corresponding

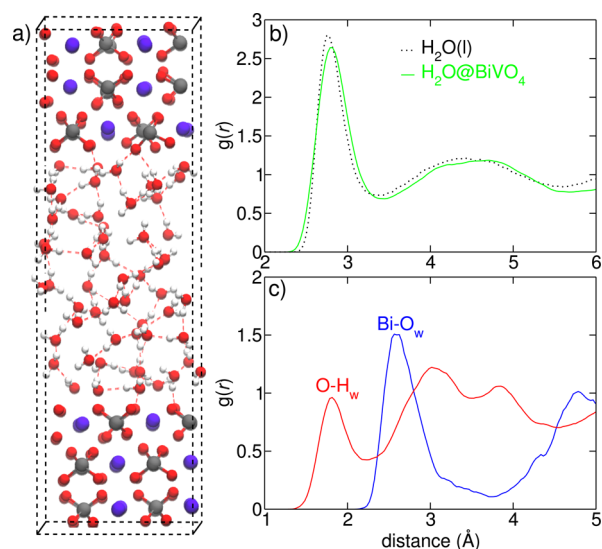


Figure 2. (a) Representation of the neutral $\text{BiVO}_4(010)$ –water interface (side view). O atoms are shown in red, H in white, Bi in purple, and V in gray. (b) O–O RDF for bulk water (black dotted) and for the bulk-like region of liquid water at the $\text{BiVO}_4(010)$ –water interface. (c) Bi_s –O and O_s –H RDFs.

to the experimental density of liquid water, following the protocol established in ref 13. To model the BiVO_4 slab, we approximate the β angle of the standard $C2/c$ monoclinic structure to 90° , close to the reported experimental value (90.43°),^{44,45} thus effectively employing the nonstandard $I2/b$ structure. We use a six-layer semiconductor slab, for which convergence in the calculated surface energy and ionization potential is achieved. We carry out MD simulations of the neutral $\text{BiVO}_4(010)$ –water interface considering two starting configurations: a molecular model, in which the water molecules are molecularly adsorbed on the semiconductor interface through a Bi–O bond and a dissociative model, in which the water molecules are dissociated on the semiconductor surface, with a hydroxyl group attached to the Bi atom and a proton bound to an O surface site. The latter is found to revert into the molecular model within 2 ps of simulation. The potential offset ΔV_w is found to converge within few ps of simulation (cf. Figure 3).

In addition, we carry out MD simulations of the adsorbates on the $\text{BiVO}_4(010)$ surface starting from the molecular model

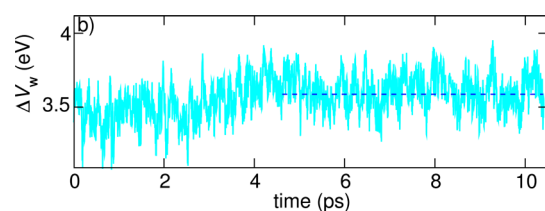


Figure 3. Time evolution of ΔV_w for the molecular $\text{BiVO}_4(010)$ –water interface. The dashed line indicates the average value.

of the interface. In particular, we carry out MD simulations of (i) the molecular $\text{BiVO}_4(010)$ –water interface where an adsorbed H_2O molecule is replaced by an hydroxyl ion and (ii) the molecular $\text{BiVO}_4(010)$ –water interface where an extra proton is added close to a surface O atom.

All MD simulations are performed with the freely available CP2K suite of codes,⁴⁶ which is based on the use of atomic basis sets and a plane-wave expansion for the electron density. Analytical Goedecker–Teter–Hutter pseudopotentials are used to account for core-valence interactions.^{47,48} We use a triple- ζ basis set for O and H atoms and double- ζ basis sets with one polarization function for Bi and V.⁴⁹ For the plane-wave basis set, a cutoff of 800 Ry is employed. The Brillouin zone is sampled at the sole Γ -point. The MD simulations are performed with the rVV10 functional, which accounts for nonlocal van der Waals interactions.^{50,51} The parameter b of the rVV10 functional is set to the value of 9.3 to correctly reproduce the density and the structural properties of liquid water.^{52,53} The MD simulations are evolved in the NVT ensemble during 10 ps for the neutral interface, following 5 ps of equilibration. For the interfaces with an adsorbed proton and an adsorbed hydroxyl ion, we use a configuration of the equilibrated neutral interface and either add a proton close to a surface O atom or remove one from an adsorbed water molecule. In these cases, we perform 5 ps MD runs after 2 ps of equilibration. We employ a time step of 0.5 fs. The temperature is set at 350 K to ensure a frank diffusive motion of liquid water and is controlled by a Nosé–Hoover thermostat.^{54,55} Hybrid functional calculations on top of the structural configurations achieved from the MD simulations are carried out with the h-rVV10 functional, developed in ref 41, which combines the PBE0 hybrid functional with the rVV10 description of nonlocal van der Waals interactions. In this functional, the fraction α of Fock exchange is set to 0.40 and the b parameter of rVV10 to 5.3.⁴¹ All hybrid functional calculations are performed using the auxiliary density matrix method that allows for a rapid evaluation of the exchange integrals through the use of a smaller auxiliary basis set.^{56,57} We here use the cFIT auxiliary basis set.^{56,57}

We first analyze the neutral $\text{BiVO}_4(010)$ –water interface. The O–O radial distribution function (RDF) calculated for H_2O molecules at a distance of least 3 Å far from the surface⁵⁸ is found to closely agree with the one calculated for the bulk liquid (cf. Figure 2b). The average Bi–O bond length for adsorbed H_2O molecules is 2.59 Å, slightly larger than the average Bi–O bond length in bulk BiVO_4 (2.45 Å). By using a cutoff distance of 3.5 Å, corresponding to the first minimum of the Bi–O(H_2O) RDF (cf. Figure 2c), we infer an average coordination number of 0.91 water molecules per Bi site. Surface O atoms are also weakly interacting with liquid water. We define, a coordination number and a hydrogen bond for a surface O atom in analogy to that of O atoms belonging to condensed-phase water molecules: (i) a 3.5 Å cutoff distance between surface O and water-molecule O atoms and (ii) an O–H–O angle larger than 140° .^{34,41} Surface O atoms are found to accept 0.53 hydrogen bonds per site on average, whereas they coordinate 2.22 water molecules. Therefore, only a small fraction of the water molecules within the coordination hemisphere donates hydrogen bonds to surface O atoms, thus indicating a low reactivity of this site. These weak interactions between water molecules and the surface sites indicate that the nature of the $\text{BiVO}_4(010)$ surface is

hydrophobic. Furthermore, we calculate the surface energy E_{surf} defined as

$$E_{\text{surf}} = \frac{E_{\text{slab}} - N_{\text{slab}} E_{\text{bulk}}}{2A_{\text{surf}}} \quad (56)$$

where E_{bulk} is the total energy of the bulk system per atom, N_{slab} is the number of atoms of the slab, and A_{surf} is the surface area. The calculated value for the $\text{BiVO}_4(010)$ is as small as $0.018 \text{ eV } \text{\AA}^{-2}$. All results are consistent with the bulk-like structure of the $\text{BiVO}_4(010)$ surface, with no relevant undercoordination of surface atoms.

The adsorption of an H^+ cation on a surface O atom (cf. Figure 4a) brings only slight structural modifications to the

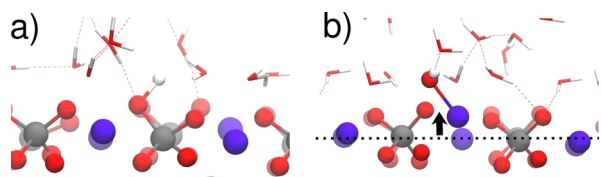
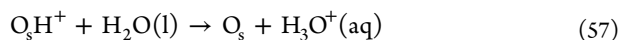


Figure 4. Representation of (a) the adsorbed H^+ cation and (b) the adsorbed OH^- anion at the $\text{BiVO}_4(010)$ surface. O atoms in red, H in white, Bi in purple, and V in gray. The dashed black line in panel (b) represents the average position of surface Bi atoms at the neutral semiconductor–water interface, whereas the black arrow represents the displacement of $0.9 \text{ \AA}$ of the surface Bi atom (see text) when an hydroxyl ion is attached to the surface. Shaded atoms represent atoms situated further from the observer.

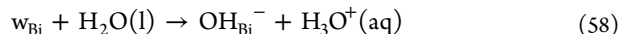
surface. The bound O atom is shifted upwards by $0.2 \text{ \AA}$ from its equilibrium position with a related elongation of the V–O bond by $0.1 \text{ \AA}$. The adsorbed proton is found to form an H bond with a water molecule of the liquid. The enhanced positive charge on the surface O atom, because of the bond with the proton, leads to slightly larger values for the number of accepted hydrogen bonds (0.90) with respect to a surface O atom not bound to H^+ (0.53). Similarly, the coordination with water molecules is found to increase from 2.22 to 2.84 . In contrast, when an adsorbed water molecule is replaced by a hydroxyl ion, the latter is found to induce a sizable surface reconstruction. In fact, the surface Bi atom is significantly displaced from its equilibrium position (by as much as $0.9 \text{ \AA}$, cf. Figure 4b). The Bi–O bond length is reduced to $2.16, 0.43 \text{ \AA}$ shorter than the Bi–O bond for a water molecule, thus indicating a stronger interaction between the adsorbate and the substrate in the case of the hydroxyl ion. The observed surface reconstruction associated with the adsorption of the hydroxyl ion can be related to the low stability observed for BiVO_4 in extreme basic conditions, in which the material has been found to dissolve.⁵⁹

4. ACIDITY OF THE $\text{BiVO}_4(010)$ SURFACE

The most stable surface of BiVO_4 is the bulk-like BiO_2 -terminated (010) surface, which is generally used in photocatalysis experiments.^{60,61} V atoms are not accessible to water molecules on this surface (cf. Figure 2a). Therefore, the only adsorption sites are Bi and O atoms. The concentration of surface O is twice that of surface Bi sites. H_2O and OH^- molecules are adsorbed on surface Bi atoms, whereas the H^+ ion is adsorbed on surface O atoms. Hence, we consider the following acid–base equilibria



and



From eq 45, $\text{pH}_{\text{PZC}}[\text{BiVO}_4(010)]$ reads as follows

$$\text{pH}_{\text{PZC}}[\text{BiVO}_4(010)] = \frac{\text{p}K_a(\text{H}_3\text{O}^+) + \text{p}K_a(\text{w}_{\text{Bi}})}{2} + 0.15 \quad (59)$$

where $\text{p}K_a(\text{H}_3\text{O}^+)$ and $\text{p}K_a(\text{H}_2\text{O}_{\text{Bi}})$ are the $\text{p}K_a$ of the H^+ on the O site and of H_2O on the Bi site, respectively, calculated from eqs 43 and 44.

In this work, the thermodynamic integrals are calculated for two values of the Kirkwood coupling parameter η (0 and 1), thus actually adopting the linear Marcus approximation. This has been found to produce a negligible error when applied to deprotonation integrals.^{34,41} Therefore, $\Delta_{\text{dp}}A_{\text{H}_3\text{O}^+}$ and $\Delta_{\text{dp}}A_{\text{w}_{\text{Bi}}}$ read as follows

$$\int_0^1 \langle \Delta_{\text{dp}}E_{\text{H}_3\text{O}^+} \rangle_{\eta} d\eta = \Delta_{\text{dp}}A_{\text{H}_3\text{O}^+} = \frac{\langle \Delta_{\text{dp}}E_{\text{H}_3\text{O}^+} \rangle_0 + \langle \Delta_{\text{dp}}E_{\text{H}_3\text{O}^+} \rangle_1}{2} \quad (60)$$

and

$$\int_0^1 \langle \Delta_{\text{dp}}E_{\text{w}_{\text{Bi}}} \rangle_{\eta} d\eta = \Delta_{\text{dp}}A_{\text{w}_{\text{Bi}}} = \frac{\langle \Delta_{\text{dp}}E_{\text{w}_{\text{Bi}}} \rangle_0 + \langle \Delta_{\text{dp}}E_{\text{w}_{\text{Bi}}} \rangle_1}{2} \quad (61)$$

$\langle \Delta_{\text{dp}}E_{\text{H}_3\text{O}^+} \rangle_0$ and $\langle \Delta_{\text{dp}}E_{\text{w}_{\text{Bi}}} \rangle_0$ are the average vertical deprotonation energies for an adsorbed proton and for a proton of an adsorbed water molecule, respectively. These quantities are calculated from a set of 200 configurations equally spaced in time and separated by 250 fs . $\langle \Delta_{\text{dp}}E_{\text{H}_3\text{O}^+} \rangle_0$ is calculated by vertical detachment of the extra adsorbed proton and $\langle \Delta_{\text{dp}}E_{\text{w}_{\text{Bi}}} \rangle_0$ by vertical detachment of a proton of an adsorbed water molecule at the neutral interface. In both cases, the proton is removed and the total energy is recalculated at fixed atoms for each configuration.

$\langle \Delta_{\text{dp}}E_{\text{H}_3\text{O}^+} \rangle_1$ and $\langle \Delta_{\text{dp}}E_{\text{w}_{\text{Bi}}} \rangle_1$ represent the energies associated with vertical proton insertion. These quantities in bulk liquid water are calculated through constrained MD simulations in which a ghost atom is kept close to the position of the acidic proton.^{34,40} Hence, the vertical insertion energy is calculated by simply switching on the nuclear charge of the ghost atom. However, in the case of a semiconductor–water interface, one should either (i) perform long MD simulations to collect significant statistics and eliminate the contributions from highly unphysical configurations (i.e., the proton below the surface or extremely close to other atoms) or (ii) add a large number of constraints, which could affect the physics of the entire system. Therefore, in this work, we propose a different and simpler method to evaluate this quantity. We perform a relaxation of the proton, which has been vertically inserted in the proximity of its acidic site. In practice, we perform a structural relaxation in which all atoms except the inserted proton are fixed. We observe that this procedure allows us to achieve converged results for the average vertical insertion energy when applied to a set of 20 structural configurations. In particular, for calculating $\langle \Delta_{\text{dp}}E_{\text{H}_3\text{O}^+} \rangle_1$, a proton is added close to an O site in structural configurations of the neutral semiconductor–water interface, whereas the calculation of $\langle \Delta_{\text{dp}}E_{\text{w}_{\text{Bi}}} \rangle_1$ implies the insertion of a proton close to the adsorbed hydroxyl ion. For solutes in an aqueous solution, this procedure has been found to bring the

same results achieved with constrained MD simulations within 0.05 eV.

We underline that our computational procedure relies on a half-reaction scheme, at variance with previous works on semiconductor–water interfaces.³¹ Our choice is motivated by the fact that finite-size effects are under control with robust correction schemes for supercells with a localized charge. Furthermore, when two half-reactions take place simultaneously in the same cell, finite-size corrections for total energies of systems with two localized charges (i.e., a proton vertically detached from a water molecule to be attached to another one, thus producing an H⁺ and an OH[−]^{31,40}) in two different positions within the supercell are subject to inaccuracies,³¹ even if this procedure preserves the charge neutrality of the supercell.

The energy of zero-point motion associated with protons for both solutes in an aqueous solution and adsorbates is estimated by calculating the vibrational frequencies of the related normal modes. In particular, we construct the displacement matrix by only considering the displacements of (i) a proton of the hydronium molecule for $\Delta_{\text{zp}}E_{\text{H}_3\text{O}^+}$, (ii) the adsorbed proton on the O site for $\Delta_{\text{zp}}E_{\text{H}_\text{O}}$, and (iii) a proton of the H₂O molecule adsorbed on a Bi site for $\Delta_{\text{zp}}E_{\text{w}_\text{Bi}}$. Therefore, for each case, we calculate three frequencies, and the zero-point energy is calculated as follows

$$\Delta_{\text{zp}}E = \sum_{n=1}^3 \frac{h\nu_i}{2} \quad (62)$$

where h is the Planck constant and ν_i is the frequency of the i -th normal mode. This computational protocol gives results for $\Delta_{\text{zp}}E_{\text{H}_3\text{O}^+}$ (cf. Table 1) in close agreement with those inferred from the experimental vibrational spectrum of the hydrated proton.^{34,62}

Table 1. Calculated Values of $\Delta\Delta_{\text{dp}}A$ (See Text for Definition), Zero-Point Energies, and pK_a of the Proton Adsorbed on an O Site, H₃O⁺, and for a Water Molecule Adsorbed on a Bi Site, w_{Bi}

		$\Delta\Delta_{\text{dp}}A$	$\Delta_{\text{zp}}E$	pK_a
H ₃ O ⁺	r	−0.09	0.29	−2.17
	h	−0.06	0.32	−1.88
w _{Bi}	r	0.63	0.31	8.20
	h	0.67	0.33	8.48
H ₃ O ⁺ (aq)	r		0.32	−1.74
	h		0.34	−1.74

^aCalculated values are obtained at both semilocal rVV10 (r) and hybrid h-rVV10 (h) levels of theory. The deprotonation integrals are referred to the deprotonation integral of a proton in aqueous hydronium at the respective level of theory.

In Table 1, we report the difference between the deprotonation integrals calculated at the interface and the deprotonation of the hydronium in bulk liquid water upon alignment, $\Delta\Delta_{\text{dp}}A$ (cf. Figure 1), zero-point energies, $\Delta_{\text{zp}}E$, and pK_a , as achieved from the MD simulations. First, we notice that acid–base constants depend mostly on the calculated deprotonation integrals. In fact, differences in zero-point energy between adsorbed species and hydronium in the bulk liquid amount to at most 0.03 eV, that is, a difference of 0.4 units in the calculated pK_a values. The pK_a calculated for the surface H⁺ (−2.17) indicates that a proton on a surface O site is slightly

more acidic than the hydronium ion (−1.74), a feature which, along with the rapid conversion of the dissociative model observed in MD simulations, is consistent with the hydrophobic and inert nature of the BiVO₄(010) in neutral conditions. In contrast, a water molecule adsorbed on the BiVO₄ surface results in a calculated pK_a of 8.2, sensitively increased with respect to the acidity of a water molecule in the bulk liquid ($pK_a = 15.74$). The bond between the Bi³⁺ site and the O atom of the water molecules allows for a partial transfer of the positive charge to the latter, which, in turn, becomes more acidic, thus favoring the release of the proton. Furthermore, the stronger interaction of the Bi site with the hydroxyl ion stabilizes the product of the reaction. When all quantities are recalculated at the hybrid functional level, we achieve pK_a values that are higher by ~0.3 pH units than those obtained at the rVV10 level. This small difference is within the accuracy of the method, thus suggesting that the semilocal functional already provides an adequate description of the deprotonation energies, as already pointed out in refs 34 and 40. We calculate the pH_{PZC} of BiVO₄(010) from eq 59, obtaining 3.25 and 3.46 at the rVV10 and h-rVV10 level, respectively. Both values compare well with the experimental range (2.5–3.5, refs 63 and 64) and are found to be in excellent agreement with the most recent experimental characterization (3.5 in ref 64). Overall, from the calculated pK_a values, we infer that the dissociation of water molecules at the BiVO₄(010) surface is clearly an unfavorable process. In fact, from eq 55, we calculate $\Delta A_d(w_\text{M}) = 0.72$ eV (0.73 eV at the h-rVV10 level of theory). This is consistent with the low reactivity and hydrophobicity of the surface.

Our microscopic characterization of the acid–base chemistry at the different surface sites enables us to describe the pH-dependent interfacial coverage of the BiVO₄(010) surface in an aqueous environment. In particular, we construct a logarithmic diagram for the concentration of all adsorbed species, similar to those commonly employed by analytical chemists in the study of weak acids in an aqueous solution. We first calculate the surface concentrations of Bi and O surface sites at the BiVO₄(010) surface, which are 6.28×10^{-9} and 1.26×10^{-8} mol/dm², respectively. Next, we employ the definition of K_a

$$K_a(\text{H}_3\text{O}^+) = \frac{[\text{H}^+(\text{aq})][\text{O}_\text{s}]}{[\text{H}_3\text{O}^+]} \quad (63)$$

and

$$K_a(w_\text{Bi}) = \frac{[\text{H}^+(\text{aq})][\text{OH}_\text{Bi}]}{[w_\text{Bi}]} \quad (64)$$

allowing for a straightforward calculation of the concentration of acid and basic species at varying pH

$$\frac{[\text{O}_\text{s}]}{[\text{H}_3\text{O}^+]} = \frac{K_a(\text{H}_3\text{O}^+)}{[\text{H}^+(\text{aq})]} \quad (65)$$

$$\frac{[\text{OH}_\text{Bi}]}{[w_\text{Bi}]} = \frac{K_a(w_\text{Bi})}{[\text{H}^+(\text{aq})]} \quad (66)$$

subject to the conditions given by

$$c_\text{Bi} = [w_\text{Bi}] + [\text{OH}_\text{Bi}] \quad (67)$$

and

$$c_\text{Bi} = [\text{H}_3\text{O}^+] + [\text{O}_\text{s}] \quad (68)$$

The diagram presented in Figure 5 provides a rapid evaluation of the microstructural properties of the surface as

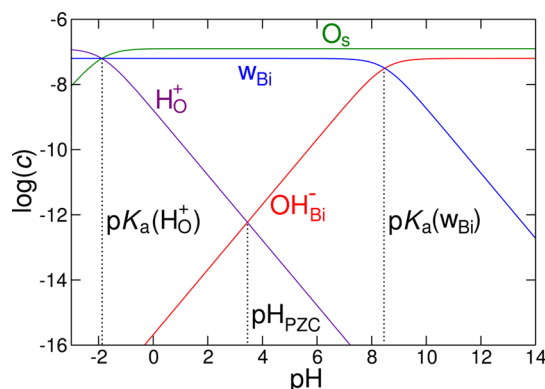


Figure 5. Acid–base logarithmic diagram for the coverage of the pristine $\text{BiVO}_4(010)$ surface in an aqueous environment, as calculated at the h-rVV10 level of theory. Concentrations are given in mol/dm^2 .

a function of pH. First, we observe that at pH_{PZC} , the concentration of ionic species is ~ 5 orders of magnitude lower than that of molecularly adsorbed water. This is in agreement with the strong preference of molecular adsorption observed in our MD simulations, thus also indicating that the employed molecular model is representative of a realistic interface at pH_{PZC} . Furthermore, we notice that a low concentration of ionic species on the surface is encountered for a large range of pH values ($1 < \text{pH} < 6$), for which the concentrations of adsorbed protons and hydroxyl ions are at about 3 order of magnitude smaller than that of molecularly adsorbed water molecules. In fact, protons are found to be present in a sizable amount only at extreme pH values. At $\text{pH} = 0$, only roughly 1% of the O surface sites are found to be protonated. At $\text{pH} = 7$, at which an ideal water-splitting plant should operate,⁶⁵ the fraction of adsorbed protons is negligible. This suggests that, even if the band alignment is favorable, the pristine BiVO_4 may be a poor photocatalyst, as the reduction of H^+ on its surface is largely adsorption limited. Furthermore, this indicates that current attempts to alter the band alignment of BiVO_4 through doping,⁶⁶ to straddle the H^+/H_2 and $\text{H}_2\text{O}/\text{O}_2$ redox potentials, may be unfruitful, as they ignore the surface chemistry of the interface. At $\text{pH} = 7$, only a small fraction of the Bi sites ($\sim 6\%$) adsorbs hydroxyl ions, and hence the water oxidation reaction should mainly proceed through the reaction mechanism occurring under acidic conditions (i.e., dehydrogenation of the adsorbed water molecules⁶⁷). More alkaline solutions may cause the hydroxylation of the surface, and the water splitting reaction may then proceed through the kinetically more favorable mechanism occurring under basic conditions (i.e., the oxidation of the adsorbed hydroxyl ion⁶⁷). However, transition-metal oxides in a strong alkaline aqueous environment can undergo corrosion, thus undermining the stability of the device.⁵⁹

A partial hydroxylation of the BiVO_4 surface in near-neutral conditions has been recently detected by X-ray ambient pressure photoelectron spectroscopy studies of the BiVO_4 –water interface.⁶⁸ However, it is not possible to directly infer the concentration of adsorbed hydroxyl ions from the spectra reported in ref 68. It should be noted that, from Figure 5, the concentration of adsorbed OH^- varies between 6 and 50% in a pH range comprised between 7 and 8.48. Furthermore, we

notice that an error as small as 0.1 eV in our calculations (which is typical for the computational protocol⁴⁰) would imply an error as large as 1.74 in the calculated pK_a values. Therefore, we can conclude that our results are consistent with the partial hydroxylation of the semiconductor surface observed in ref 68 within the accuracy of the method.

5. CONCLUSIONS

In this work, we developed a theoretical formulation to study the pH-dependent interfacial coverage of semiconductor–water interfaces. In particular, we employed a grand-canonical formulation for solutes in an aqueous solution and adsorbed species at the interface. The proposed method has been supplemented with computational protocols based on electronic structure calculations, MD simulations, and the thermodynamic integration method. Applied to the $\text{BiVO}_4(010)$ –water interface, our scheme implies three MD simulations: (i) the neutral $\text{BiVO}_4(010)$ –water interface, (ii) the positively charged interface with an extra adsorbed proton on a surface O atom, and (iii) the negatively charged interface in which an adsorbed water molecule is replaced by an hydroxyl anion. Water molecules were found to be adsorbed molecularly on the $\text{BiVO}_4(010)$ surface through weak interactions with surface Bi sites. At variance, the hydroxyl ion featured strong interactions with surface Bi^{3+} , as inferred from the noticeable shortening of the Bi–O bond length. The analysis of the acid–base properties at the surface revealed that surface O sites are extremely acidic, the pK_a of the adsorbed proton being close to that of the hydronium ion in bulk water. In contrast, the acidity of the adsorbed water molecule was found to be sensitively increased with respect to that of the condensed-phase molecule, as a consequence of the metal–oxygen charge transfer. Overall, from the pK_a values of the individual sites, we achieved a pH_{PZC} in excellent agreement with the experimental characterization. Furthermore, from the calculated pK_a of the individual adsorption sites, we constructed an ab initio concentration diagram of all species at the interface as a function of the pH of the aqueous solution. This enabled us to get deeper insight into the pH-dependent coverage of the semiconductor–water interface. In particular, we noticed that a sizable fraction of O sites ($\sim 6\%$) is occupied by protons only in highly acidic conditions ($\text{pH} = 0$). This suggests that recent efforts to modulate the band alignment of BiVO_4 through doping to have its band gap straddle both the water redox levels could be unfruitful. In contrast, we observed that the hydroxyl ion is attached to the $\text{BiVO}_4(010)$ surface in sizable concentrations ($\sim 1\%$ of Bi sites) already at $\text{pH} = 7$ and is the dominant adsorbed species in highly basic conditions, where it may lead to the corrosion and dissolution of the material, as has been observed experimentally.⁵⁹

In conclusion, the characterization of the pH-dependent surface chemistry at semiconductor–water interfaces is a key feature to assess the properties of such interfaces. Deposition of overlayers or clusters on the surface may alter the chemistry of the interface and thereby influence the reaction mechanisms. The possible changes in the surface chemistry induced by surface modifications should be accounted for when designing new device architectures.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Francesco.Ambrosio@epfl.ch. Phone: +41 21 6933423. Fax: +41 21 693 5419.

ORCID

Francesco Ambrosio: 0000-0002-6388-9586

Julia Wiktor: 0000-0003-3395-1104

Alfredo Pasquarello: 0000-0002-9142-2799

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been performed in the context of the National Center of Competence in Research (NCCR): Materials' Revolution: Computational Design and Discovery of Novel Materials (MARVEL) of the Swiss National Science Foundation. We used computational resources of the Swiss National Supercomputing Center (CSCS) and of SCITA-SEPFL.

REFERENCES

- (1) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.
- (2) Khan, S. U. M.; Al-Shahry, M.; Ingler, W. B., Jr. Efficient Photochemical Water Splitting by a Chemically Modified n-TiO₂. *Science* **2002**, *297*, 2243–2245.
- (3) Kudo, A.; Miseki, Y. Heterogeneous Photocatalyst Materials for Water Splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278.
- (4) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* **2010**, *110*, 6446–6473.
- (5) Liu, J.; Liu, Y.; Liu, N.; Han, Y.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S.-T.; Zhong, J.; Kang, Z. Metal-free Efficient Photocatalyst for Stable Visible Water Splitting via a Two-electron Pathway. *Science* **2015**, *347*, 970–974.
- (6) Luo, J.; Im, J.-H.; Mayer, M. T.; Schreier, M.; Nazeeruddin, M. K.; Park, N.-G.; Tilley, S. D.; Fan, H. J.; Grätzel, M. Water Photolysis at 12.3% Efficiency via Perovskite Photovoltaics and Earth-abundant Catalysts. *Science* **2014**, *345*, 1593–1596.
- (7) Castelli, I. E.; Olsen, T.; Datta, S.; Landis, D. D.; Dahl, S.; Thygesen, K. S.; Jacobsen, K. W. Computational Screening of Perovskite Metal Oxides for Optimal Solar Light Capture. *Energy Environ. Sci.* **2012**, *5*, 5814–5819.
- (8) Castelli, I. E.; Landis, D. D.; Thygesen, K. S.; Dahl, S.; Chorkendorff, I.; Jaramillo, T. F.; Jacobsen, K. W. New Cubic Perovskites for One- and Two-photon Water Splitting Using the Computational Materials Repository. *Energy Environ. Sci.* **2012**, *5*, 9034–9043.
- (9) Zhuang, H. L.; Hennig, R. G. Single-Layer Group-III Monochalcogenide Photocatalysts for Water Splitting. *Chem. Mater.* **2013**, *25*, 3232–3238.
- (10) Wu, Y.; Chan, M. K. Y.; Ceder, G. Prediction of Semiconductor Band Edge Positions in Aqueous Environments from First Principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *83*, 235301.
- (11) Wu, Y.; Lazic, P.; Hautier, G.; Persson, K.; Ceder, G. First Principles High Throughput Screening of Oxynitrides for Water-splitting Photocatalysts. *Energy Environ. Sci.* **2013**, *6*, 157–168.
- (12) Katz, J. E.; Gingrich, T. R.; Santori, E. A.; Lewis, N. S. Combinatorial Synthesis and High-throughput Photopotential and Photocurrent Screening of Mixed-metal Oxides for Photoelectrochemical Water Splitting. *Energy Environ. Sci.* **2009**, *2*, 103–112.
- (13) Guo, Z.; Ambrosio, F.; Chen, W.; Gono, P.; Pasquarello, A. Alignment of Redox Levels at Semiconductor–Water Interfaces. *Chem. Mater.* **2018**, *30*, 94–111.
- (14) Peterson, A. A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J. K. How Copper Catalyzes the Electroreduction of Carbon Dioxide into Hydrocarbon Fuels. *Energy Environ. Sci.* **2010**, *3*, 1311–1315.
- (15) Kudo, A.; Omori, K.; Kato, H. A Novel Aqueous Process for Preparation of Crystal Form-Controlled and Highly Crystalline BiVO₄ Powder from Layered Vanadates at Room Temperature and Its Photocatalytic and Photophysical Properties. *J. Am. Chem. Soc.* **1999**, *121*, 11459–11467.
- (16) Yu, J.; Kudo, A. Effects of Structural Variation on the Photocatalytic Performance of Hydrothermally Synthesized BiVO₄. *Adv. Funct. Mater.* **2006**, *16*, 2163–2169.
- (17) Luo, H.; Mueller, A. H.; McCleskey, T. M.; Burrell, A. K.; Bauer, E.; Jia, Q. X. Structural and Photoelectrochemical Properties of BiVO₄ Thin Films. *J. Phys. Chem. C* **2008**, *112*, 6099–6102.
- (18) Park, Y.; McDonald, K. J.; Choi, K.-S. Progress in Bismuth Vanadate Photoanodes for Use in Solar Water Oxidation. *Chem. Soc. Rev.* **2013**, *42*, 2321–2337.
- (19) Kim, T. W.; Choi, K.-S. Nanoporous BiVO₄ Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. *Science* **2014**, *343*, 990–994.
- (20) Ma, Y.; Le Formal, F.; Kafizas, A.; Pendlebury, S. R.; Durrant, J. R. Efficient Suppression of Back Electron/Hole Recombination in Cobalt Phosphate Surface-modified Undoped Bismuth Vanadate Photoanodes. *J. Mater. Chem. A* **2015**, *3*, 20649–20657.
- (21) Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. Nickel–Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: The Role of Intentional and Incidental Iron Incorporation. *J. Am. Chem. Soc.* **2014**, *136*, 6744–6753.
- (22) Zhong, D. K.; Choi, S.; Gamelin, D. R. Near-Complete Suppression of Surface Recombination in Solar Photoelectrolysis by “Co-Pi” Catalyst-Modified W:BiVO₄. *J. Am. Chem. Soc.* **2011**, *133*, 18370–18377.
- (23) Zachäus, C.; Abdi, F. F.; Peter, L. M.; van de Krol, R. Photocurrent of BiVO₄ is limited by surface recombination, not surface catalysis. *Chem. Sci.* **2017**, *8*, 3712–3719.
- (24) Hiemstra, T.; Van Riemsdijk, W. H.; Bolt, G. H. Multisite Proton Adsorption Modeling at the Solid/Solution Interface of (Hydr)oxides: A New Approach: I. Model Description and Evaluation of Intrinsic Reaction Constants. *J. Colloid Interface Sci.* **1989**, *133*, 91–104.
- (25) Hiemstra, T.; Venema, P.; Van Riemsdijk, W. H. Intrinsic Proton Affinity of Reactive Surface Groups of Metal (Hydr)oxides: The Bond Valence Principle. *J. Colloid Interface Sci.* **1996**, *184*, 680–692.
- (26) Sverjensky, D. A.; Sahai, N. Theoretical Prediction of Single-Site Surface-Protonation Equilibrium Constants for Oxides and Silicates in Water. *Geochim. Cosmochim. Acta* **1996**, *60*, 3773–3797.
- (27) Machesky, M. L.; Wesolowski, D. J.; Palmer, D. A.; Ridley, M. K. On the Temperature Dependence of Intrinsic Surface Protonation Equilibrium Constants: An Extension of the Revised MUSIC Model. *J. Colloid Interface Sci.* **2001**, *239*, 314–327.
- (28) Sahai, N. Is Silica Really an Anomalous Oxide? Surface Acidity and Aqueous Hydrolysis Revisited. *Environ. Sci. Technol.* **2002**, *36*, 445–452.
- (29) Bickmore, B. R.; Tadanier, C. J.; Rosso, K. M.; Monn, W. D.; Eggett, D. L. Bond-valence Methods for pKa Prediction: Critical Reanalysis and New Approach. *Geochim. Cosmochim. Acta* **2004**, *68*, 2025–2042.
- (30) Bickmore, B. R.; Rosso, K. M.; Tadanier, C. J.; Bylaska, E. J.; Doud, D. Bond-valence Methods for pKa Prediction. II. Bond-valence, Electrostatic, Molecular Geometry, and Solvation Effects. *Geochim. Cosmochim. Acta* **2006**, *70*, 4057–4071.
- (31) Cheng, J.; Sprik, M. Acidity of the Aqueous Rutile TiO₂(110) Surface from Density Functional Theory Based Molecular Dynamics. *J. Chem. Theory Comput.* **2010**, *6*, 880–889.
- (32) Sulpizi, M.; Gageot, M.-P.; Sprik, M. The Silica–Water Interface: How the Silanols Determine the Surface Acidity and Modulate the Water Properties. *J. Chem. Theory Comput.* **2012**, *8*, 1037–1047.
- (33) Liu, X.; Lu, X.; Cheng, J.; Sprik, M.; Wang, R. Temperature Dependence of Interfacial Structures and Acidity of Clay Edge Surfaces. *Geochim. Cosmochim. Acta* **2015**, *160*, 91–99.
- (34) Ambrosio, F.; Miceli, G.; Pasquarello, A. Redox Levels in Aqueous Solution: Effect of van der Waals Interactions and Hybrid Functionals. *J. Chem. Phys.* **2015**, *143*, 244508.

- (35) Freysoldt, C.; Neugebauer, J.; Van de Walle, C. G. Fully Ab Initio Finite-Size Corrections for Charged-Defect Supercell Calculations. *Phys. Rev. Lett.* **2009**, *102*, 016402.
- (36) Komsa, H.-P.; Rantala, T. T.; Pasquarello, A. Finite-size Supercell Correction Schemes for Charged Defect Calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 045112.
- (37) Freysoldt, C.; Grabowski, B.; Hickel, T.; Neugebauer, J.; Kresse, G.; Janotti, A.; Van de Walle, C. G. First-principles Calculations for Point Defects in Solids. *Rev. Mod. Phys.* **2014**, *86*, 253–305.
- (38) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Academic Press: San Diego, 2002.
- (39) Kirkwood, J. G. Statistical Mechanics of Fluid Mixtures. *J. Chem. Phys.* **1935**, *3*, 300–313.
- (40) Cheng, J.; Sprik, M. Alignment of Electronic Energy Levels at Electrochemical Interfaces. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11245–11267.
- (41) Ambrosio, F.; Miceli, G.; Pasquarello, A. Structural, Dynamical, and Electronic Properties of Liquid Water: a Hybrid Functional Study. *J. Phys. Chem. B* **2016**, *120*, 7456–7470.
- (42) Todorova, M.; Neugebauer, J. Extending the Concept of Defect Chemistry from Semiconductor Physics to Electrochemistry. *Phys. Rev. Appl.* **2014**, *1*, 014001.
- (43) Komsa, H.-P.; Pasquarello, A. Finite-Size Supercell Correction for Charged Defects at Surfaces and Interfaces. *Phys. Rev. Lett.* **2013**, *110*, 095505.
- (44) Oshikiri, M.; Boero, M. Water Molecule Adsorption Properties on the $\text{BiVO}_4(100)$ Surface. *J. Phys. Chem. B* **2006**, *110*, 9188–9194.
- (45) Oshikiri, M.; Boero, M.; Matsushita, A.; Ye, J. Water Molecule Adsorption Properties on Surfaces of MVO_4 ($\text{M} = \text{In}, \text{Y}, \text{Bi}$) Photocatalysts. *J. Electroceram.* **2009**, *22*, 114–119.
- (46) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and Accurate Density Functional Calculations using a Mixed Gaussian and Plane Waves Approach. *Comput. Phys. Commun.* **2005**, *167*, 103–128.
- (47) Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-space Gaussian pseudopotentials. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 1703–1710.
- (48) Hartwigsen, C.; Goedecker, S.; Hutter, J. Relativistic separable dual-space Gaussian pseudopotentials from H to Rn. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *58*, 3641–3662.
- (49) VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *J. Chem. Phys.* **2007**, *127*, 114105.
- (50) Vydrov, O. A.; Van Voorhis, T. Nonlocal van der Waals Density Functional: The Simpler the Better. *J. Chem. Phys.* **2010**, *133*, 244103.
- (51) Sabatini, R.; Gorni, T.; de Gironcoli, S. Nonlocal van der Waals Density Functional Made Simple and Efficient. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 041108.
- (52) Miceli, G.; de Gironcoli, S.; Pasquarello, A. Isobaric First-principles Molecular Dynamics of Liquid Water with Nonlocal van der Waals Interactions. *J. Chem. Phys.* **2015**, *142*, 034501.
- (53) Miceli, G.; Hutter, J.; Pasquarello, A. Liquid Water through Density-Functional Molecular Dynamics: Plane-Wave vs Atomic-Orbital Basis Sets. *J. Chem. Theory Comput.* **2016**, *12*, 3456–3462.
- (54) Nosé, S. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. *J. Chem. Phys.* **1984**, *81*, 511–519.
- (55) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31*, 1695–1697.
- (56) Guidon, M.; Hutter, J.; VandeVondele, J. Robust Periodic Hartree–Fock Exchange for Large-Scale Simulations Using Gaussian Basis Sets. *J. Chem. Theory Comput.* **2009**, *5*, 3010–3021.
- (57) Guidon, M.; Hutter, J.; VandeVondele, J. Auxiliary Density Matrix Methods for Hartree–Fock Exchange Calculations. *J. Chem. Theory Comput.* **2010**, *6*, 2348–2364.
- (58) Kaya, S.; Schlesinger, D.; Yamamoto, S.; Newberg, J. T.; Bluhm, H.; Ogasawara, H.; Kendelewicz, T.; Brown, G. E.; Pettersson, L. G. M.; Nilsson, A. Highly Compressed Two-Dimensional Form of Water at Ambient Conditions. *Sci. Rep.* **2013**, *3*, 1074.
- (59) Kim, T. W.; Choi, K.-S. Improving Stability and Photoelectrochemical Performance of BiVO_4 Photoanodes in Basic Media by Adding a ZnFe_2O_4 Layer. *J. Phys. Chem. Lett.* **2016**, *7*, 447–451.
- (60) Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C. Spatial Separation of Photogenerated Electrons and Holes among $\{010\}$ and $\{110\}$ Crystal Facets of BiVO_4 . *Nat. Commun.* **2013**, *4*, 1432.
- (61) Zhao, Z.; Li, Z.; Zou, Z. Structure and Energetics of Low-Index Stoichiometric Monoclinic Clinobisvanite BiVO_4 Surfaces. *RSC Adv.* **2011**, *1*, 874.
- (62) Kim, J.; Schmitt, U. W.; Gruetzmacher, J. A.; Voth, G. A.; Scherer, N. E. The vibrational spectrum of the hydrated proton: Comparison of experiment, simulation, and normal mode analysis. *J. Chem. Phys.* **2002**, *116*, 737–746.
- (63) Castillo, N. C.; Heel, A.; Graule, T.; Pulgarin, C. Flame-assisted Synthesis of Nanoscale, Amorphous and Crystalline, Spherical BiVO_4 with Visible-light Photocatalytic Activity. *Appl. Catal., B* **2010**, *95*, 335–347.
- (64) Obregón, S.; Colón, G. On the Different Photocatalytic Performance of BiVO_4 Catalysts for Methylene Blue and Rhodamine B Degradation. *J. Mol. Catal. A: Chem.* **2013**, *376*, 40–47.
- (65) Tachibana, Y.; Vayssieres, L.; Durrant, J. R. Artificial Photosynthesis for Solar Water-Splitting. *Nat. Photonics* **2012**, *6*, 511–518.
- (66) Jo, W. J.; Kang, H. J.; Kong, K.-J.; Lee, Y. S.; Park, H.; Lee, Y.; Buonassisi, T.; Gleason, K. K.; Lee, J. S. Phase transition-induced Band Edge Engineering of BiVO_4 to Split Pure Water Under Visible Light. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 13774–13778.
- (67) Koper, M. T. M. Theory of Multiple Proton–electron Transfer Reactions and its Implications for Electrocatalysis. *Chem. Sci.* **2013**, *4*, 2710–2723.
- (68) Starr, D. E.; Favaro, M.; Abdi, F. F.; Bluhm, H.; Crumlin, E. J.; van de Krol, R. Combined soft and hard X-ray ambient pressure photoelectron spectroscopy studies of semiconductor/electrolyte interfaces. *J. Electron Spectrosc. Relat. Phenom.* **2017**, *221*, 106–115.