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pH-dependent surface chemistry from
first-principles: Application to the
 $\text{BiVO}_4(010)$ -water interface

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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 $\text{p}K_{\text{a}}$ values of the individual adsorption sites, we construct an *ab initio* concentration diagram of all the 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.

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, the photocatalyst is instrumental in determining the efficiency of the 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, i.e. band gap and band edges^{7–9,11–13} or on the overpotentials associated

with the multi-step water oxidation reaction.¹⁴ However, simplified computational protocols, i.e. lack of explicit solvent, use of 0 K structural models, 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 elude even the experimental characterization. In 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 these variables in a single simulation is possibly beyond reach.

Even if one considers the simplest case, i.e. 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 favour 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 favoured 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, i.e. 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 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

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3 interfaces have proved not to be always sufficient to discern between molecular and disso-
4 ciative adsorption of water molecules on the semiconductor surface.¹³ Therefore, an analysis
5 of the structural properties at semiconductor-water interfaces based on direct simulations is
6 sometimes not actually feasible. Nevertheless, this piece of information is instrumental to
7 understand the mechanism of heterogeneous water-splitting. For instance, BiVO₄, one of
8 the most promising materials for water splitting,^{15–18} has its intrinsic photocatalytic prop-
9 erties far from being understood.^{18–23} In particular, recent measurements indicate, contrary
10 to previous assumptions that the efficiency of water splitting on this semiconductor is rather
11 promising, even without deposition of a catalyst on the surface.²³

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

43 We here present a general formulation to study the pH-dependent interfacial coverage of
44 semiconductor-water interfaces based on a grand-canonical formulation for solutes in aqueous
45 solution and species adsorbed on the surface. The proposed theoretical framework combined
46 with specific computational protocols based on *ab initio* MD simulations allows us to ac-
47 curately calculate the pH at the point of zero charge, pH_{PZC}, for a generic surface and the
48 acidity of its various adsorption sites. This method is applied to the study of the inter-
49 face between water and BiVO₄. By modeling the adsorption of H₂O, H⁺, and OH[−] at the
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BiVO₄(010)-water interface, we yield a pH_{PZC} in excellent agreement with 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 the species at the interface as a function of the pH of the aqueous solution. The implication 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 aqueous environment and discuss the calculated pH_{PZC} and the pK_a of the surface adsorption sites. The conclusions are drawn in Section 5.

2 Theory

2.1 Grand-canonical formulation for solutes in aqueous solution

The formation Gibbs free energy of a solute X in a charge state q is given by:³⁴

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

where $G^q[X]$ is the Gibbs free energy of the solute X in the charged state q , $G[\text{bulk}]$ the Gibbs free energy of bulk water, μ_i the chemical potential of the added/subtracted species i , n_i the number of added/subtracted i atoms, $\varepsilon_{\text{v-w}}$ the valence band edge of bulk liquid water, μ_e the electron chemical potential, and E_{corr}^q a correction term taking into account electrostatic finite-size effects. In this work, the Freysoldt-Neugebauer-Van de Walle (FNV) 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

(H_3O^+ and OH^-) in a periodic supercell containing 64 water molecules, corrections to total energies are as small as 0.03 eV, due to the high dielectric constant of liquid water at ambient conditions (78.3). In this formulation, the redox level $\mu_e(q/q')$ 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.

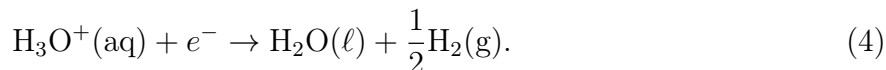
The thermodynamic integration method is used to calculate free energy differences. In this technique, an auxiliary Hamiltonian is defined as a linear combination of the Hamiltonians of the reactant and the product:^{38,39}

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

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 integration of the $\langle \Delta E \rangle_\eta$ calculated at varying η :

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

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 expression:³⁴

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

where:

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

$\Delta_{\text{dp}} A_{\text{H}_3\text{O}^+}$ is the integral associated to the deprotonation reaction of the hydronium cation, $\Delta_{\text{zp}} E_{\text{H}_3\text{O}^+}$ a correction that accounts for the lack of nuclear quantum motions in our MD simulations, and μ_{H} 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 liter of liquid water (55.5 mol/l), T the temperature, and k_{B} 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:

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

Therefore, we combine Eqs. (8) and (9) and isolate μ_e :

$$\mu_e = \Delta_{dp}A_{H_3O^+} - \Delta_{zp}E_{H_3O^+} + \mu_H - \varepsilon_{v-w} - E_{corr}^{+1} + k_B T(\ln c_0 + \ln 10 \cdot \text{pH}). \quad (10)$$

It should be noted that the chemical potentials of the hydrogen atom, the proton, and the electron are related through the following expression:⁴²

$$\mu_H = \mu_e + \mu_{H^+}, \quad (11)$$

By substituting Eq. (11) into Eq. (10), we obtain the following expression:

$$\mu_{H^+} = -\Delta_{dp}A_{H_3O^+} + \Delta_{zp}E_{H_3O^+} + \varepsilon_{v-w} + E_{corr}^{+1} - k_B T(\ln c_0 + \ln 10 \cdot \text{pH}), \quad (12)$$

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 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, $c_{H^+}(\text{ads})$ is equal to that of adsorbed hydroxyl ions, $c_{OH^-}(\text{ads})$:

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

$c_{H^+}(\text{ads})$ and $c_{OH^-}(\text{ads})$ 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:

$$c_{H^+}(\text{ads}) = \sum_{i=1}^N c_{H^+}(i) = \sum_{i=1}^N c_i e^{-G_f[H^+]_i/k_B T}, \quad (14)$$

and

$$c_{\text{OH}^-}(\text{ads}) = \sum_{i=1}^N c_{\text{OH}^-}(i) = \sum_{i=1}^N c_i e^{-G_f[\text{OH}^-]_i/k_B T}, \quad (15)$$

where the sum runs over the number N of non-equivalent adsorption sites at the surface, c_i is the surface concentration of the adsorption site i , and $G_f[\text{H}^+]_i$ and $G_f[\text{OH}^-]_i$ 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 the 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 a non-metal site. We also assume that all M and A sites are equivalent and that H^+ is adsorbed only on the A sites, while 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:

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

and

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

where $G_f[\text{H}^+]_{\text{M}}$, $G_f[\text{OH}^-]_{\text{M}}$, $G_f[\text{H}^+]_{\text{A}}$, and $G_f[\text{OH}^-]_{\text{A}}$ 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:

$$c_{\text{H}^+}(\text{ads}) = c_{\text{A}} e^{-G_f[\text{H}^+]_{\text{A}}/k_B T}, \quad (18)$$

and

$$c_{\text{OH}^-}(\text{ads}) = c_{\text{M}} e^{-G_f[\text{OH}^-]_{\text{M}}/k_B T}. \quad (19)$$

At the pH of zero-point charge [cf. Eq. (13)]:

$$c_A e^{-G_f[H^+]_A/k_B T} = c_M e^{-G_f[OH^-]_M/k_B T}. \quad (20)$$

$G_f[H^+]_A$ and $G_f[OH^-]_M$ 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 aqueous solution. We hence define the Gibbs free energy of formation of an adsorbate Y in the charged state q , as follows:

$$G_f^q[Y] = G^q[Y] - G[\text{ref}] - \sum_i n_i \mu_i + q[\varepsilon_{v-w}(\text{int}) + \mu_e] + E_{\text{corr}}^q(\text{int}), \quad (21)$$

where $G^q[Y]$ is the Gibbs free energy of the adsorbate Y in the charged state q , $G[\text{ref}]$ the Gibbs free energy of the reference interface system, μ_i the chemical potential of the added/subtracted species i , n_i the number of added/subtracted atoms of the i -th atomic species (positive for added species, negative for subtracted species), $\varepsilon_{v-w}(\text{int})$ the valence band edge of liquid water at the interface with the semiconductor, μ_e the electron chemical potential, and $E_{\text{corr}}^q(\text{int})$ 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. Due to the high dielectric constants of both BiVO_4 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. $\varepsilon_v(\text{int})$ can be related to ε_{v-w} through:

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

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. Fig. 1). Substituting in Eq. (21), we obtain:

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

The formation free energies of adsorbed H^+ and OH^- read as follows:

$$G_f[\text{H}^+]_A = G[\text{H}^+]_A - G[\text{ref}] - \mu_H + \varepsilon_{v-w} - \Delta V_w + \mu_e + E_{\text{corr}}^{+1}(\text{int}), \quad (25)$$

and

$$G_f[\text{OH}^-]_M = G[\text{OH}^-]_M - G[\text{ref}] + \mu_H - \varepsilon_{v-w} + \Delta V_w - \mu_e + E_{\text{corr}}^{-1}(\text{int}). \quad (26)$$

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 to the deprotonation reaction of a proton adsorbed on a surface A site 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:

$$\begin{aligned} 2\mu_e = & \Delta_{\text{dp}} A_{\text{wM}} + \Delta_{\text{dp}} A_{\text{H}_A^+} + 2\mu_{\text{H}} - \Delta_{\text{zp}} E_{\text{wM}} - \Delta_{\text{zp}} E_{\text{H}_A^+} \\ & - 2\varepsilon_{\text{v-w}} + 2\Delta V_{\text{w}} + E_{\text{corr}}^{-1}(\text{int}) - E_{\text{corr}}^{+1}(\text{int}) - k_B T \ln \left(\frac{c_M}{c_A} \right). \end{aligned} \quad (30)$$

We hence replace μ_e with the definition provided in Eq. (10), thus effectively achieving an expression for pH_{PZC} :

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

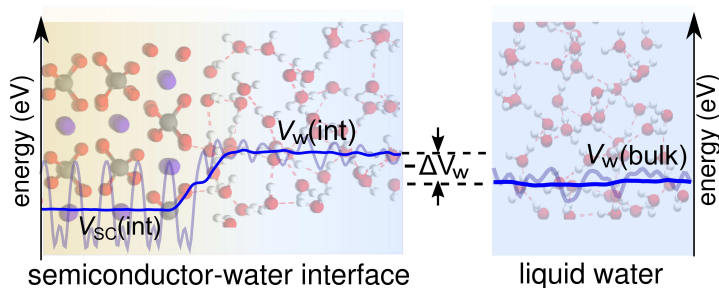


Figure 1: Schematic representation of the alignment scheme. The line-up between the average electrostatic potential in bulk liquid water $V_{\text{w}}(\text{bulk})$ and at the semiconductor-water interface $V_{\text{w}}(\text{int})$ is achieved through ΔV_{w} [cf. Eq. (23)].

2.4 Acidity of molecules at the adsorption site

Calculated values of pH_{PZC} allow for a straightforward comparison with 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

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

From Eqs. (34–37), μ_e reads as follows:

$$\mu_e = G[B^-]_i - G[HB]_i + \mu_H - \varepsilon_{v-w} + \Delta V_w + E_{\text{corr}}^{-1}(\text{int}), \quad (38)$$

where

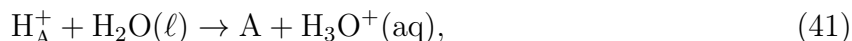
$$\begin{aligned} G[B^-]_i - G[HB]_i &= \int_0^1 \langle \Delta_{\text{dp}} E_{\text{HB}_i} \rangle_\eta d\eta - \Delta_{\text{zp}} E_{\text{HB}_i} \\ &= \Delta_{\text{dp}} A_{\text{HB}_i} - \Delta_{\text{zp}} E_{\text{HB}_i} \end{aligned} \quad (39)$$

is the thermodynamic integral associated to the deprotonation of the adsorbed HB molecule.

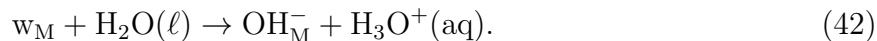
By replacing μ_e with Eq. (10), we obtain $\text{p}K_a(\text{HB}_i)$:

$$\begin{aligned} \text{p}K_a(\text{HB}_i) &= \frac{\Delta_{\text{dp}} A_{\text{HB}_i} - \Delta_{\text{dp}} A_{\text{H}_3\text{O}^+} + \Delta V_w}{\ln 10 k_B T} \\ &\quad + \frac{-\Delta_{\text{zp}} E_{\text{HB}_i} + \Delta_{\text{zp}} E_{\text{H}_3\text{O}^+}}{\ln 10 k_B T} \\ &\quad + \frac{E_{\text{corr}}^{-1}(\text{int}) + E_{\text{corr}}^{+1}}{\ln 10 k_B T} - \log c_0, \end{aligned} \quad (40)$$

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 $\text{p}K_a$ of H^+

adsorbed on A and of OH^- adsorbed on M, respectively:

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

and

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

From Eqs. (31), (43), and (44), pH_{PZC} reads as follows:

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

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:

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

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

$$K_d(w_M) = e^{-(G_f[OH^-]_M + G_f[H^+]_A - G_f[w]_M - G_f[A])/k_B T}, \quad (48)$$

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

$$\Delta A_d(w_M) = G_f[OH^-]_M + G_f[H^+]_A - G_f[w]_M - G_f[A], \quad (49)$$

we then obtain from Eq. (48):

$$K_d(w_M) = e^{-\Delta A_d(w_M)/k_B T}, \quad (50)$$

and

$$\Delta A_d(w_M) = -k_B T \ln K_d(w_M) = -k_B T \ln 10 \cdot \log K_d(w_M). \quad (51)$$

From Eqs. (41) and (42), we have:

$$K_a(H_A^+) = \frac{[A][H_3O^+(aq)]}{[H_A^+]}, \quad (52)$$

and

$$K_a(w_M) = \frac{[OH^-]_M [H_3O^+(aq)]}{[w_M]}. \quad (53)$$

From Eqs. (47), (52), and (53), we can express $K_d(w_M)$ from $K_a(H_A^+)$ and $K_a(w_M)$:

$$K_d(w_M) = \frac{K_a(w_M)}{K_a(H_A^+)}. \quad (54)$$

Therefore, from Eqs. (51) and (54) the free energy of dissociation of an adsorbed water molecule reads as follows:

$$\Delta A_d(w_M) = \ln 10 \cdot k_B T [\text{p}K_a(w_M) - \text{p}K_a(\text{H}_A^+)]. \quad (55)$$

3 Molecular dynamics simulations of BiVO₄(010)-water interfaces

We model the neutral BiVO₄(010)-water interface with an orthorhombic supercell [$a = 10.39$, $b = 10.18$, and $c = 36.17$ Å, cf. Fig. 2(a)] containing 56 H₂O molecules and corresponding to the experimental density of liquid water, following the protocol established in Ref. 13. To model the BiVO₄ 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 BiVO₄ (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. Fig. 3].

In addition, we carry out MD simulations of the adsorbates on the BiVO₄(010) surface starting from the molecular model of the interface. In particular, we carry out MD simulations of (i) the molecular BiVO₄(010)-water interface where an adsorbed H₂O molecule is replaced by an hydroxyl ion, (ii) the molecular BiVO₄(010)-water interface where an extra proton is added close to a surface O atom.

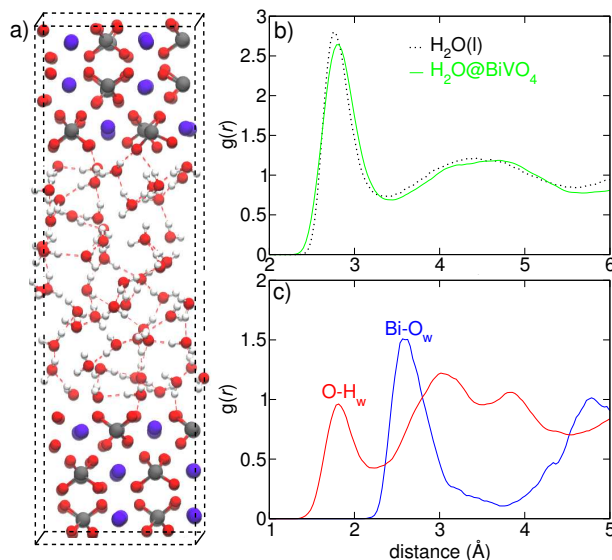


Figure 2: (a) Representation of the neutral $\text{BiVO}_4(010)$ -water interface (side view). O atoms are shown in red, H in white, Bi in purple, and V in grey. (b) O-O radial distribution function (RDF) for bulk water (black dotted) and for the bulk-like region of liquid water at the $\text{BiVO}_4(010)$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

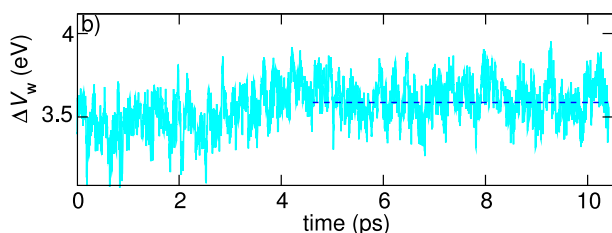


Figure 3: Time evolution of ΔV_w for the molecular $\text{BiVO}_4(010)$ -water interface. The dashed line indicates the average value.

All the 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, in order 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 the hybrid-functional calculations are performed using the auxiliary density matrix method which 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 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. Fig. 2(b)]. 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 cut-off distance of 3.5 Å, corresponding to the first minimum of the Bi-O(H_2O) RDF [cf. Fig. 2(b)], 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, while they coordinate 2.22 water molecules. Therefore, only a small fraction of the water molecules within the coordination hemisphere donate 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} the number of atoms of the slab, A_{surf} the surface area. The calculated value for the $\text{BiVO}_4(010)$ is as small as $0.018 \text{ eV}\text{\AA}^{-2}$. All these 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 a H^+ cation on a surface O atom [cf. Fig. 4(a)] brings only slight structural modifications to the 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 a H-bond with a water molecule of the liquid. The enhanced positive charge on the surface O atom, due to 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 an 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. Fig. 4(b)]. The Bi-O bond length is reduced to $2.16 \text{ \AA}$, $0.43 \text{ \AA}$ 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 to 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

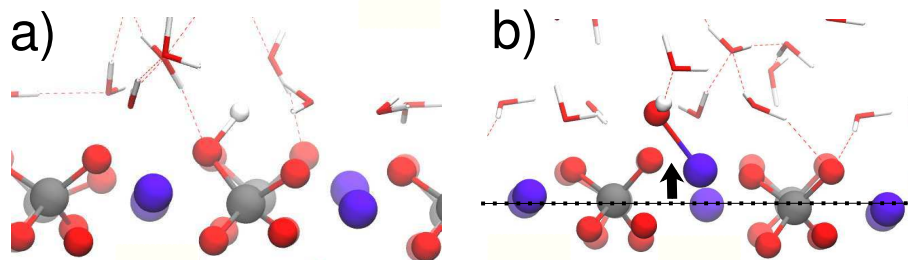
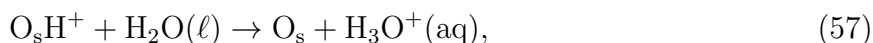


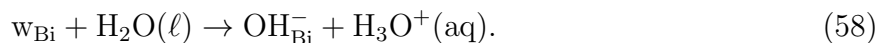
Figure 4: Representation of (a) the adsorbed H^+ cation and (b) the adsorbed OH^- anion on the $\text{BiVO}_4(010)$ surface. O atoms in red, H in white, Bi in purple, and V in grey. The dashed black line in panel (b) represents the average position of a surface Bi site at the neutral semiconductor-water interface, while 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 represents atoms situated further from the observer.

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. Fig. 2(a)]. 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, while 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:

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

where $\text{p}K_a(\text{H}_\text{O}^+)$ 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, $\Delta_{\text{dp}}A_{\text{H}_\text{O}^+}$ and $\Delta_{\text{dp}}A_{\text{wBi}}$ read as follows:

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

and

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

$\langle \Delta_{\text{dp}}E_{\text{H}_\text{O}^+} \rangle_0$ and $\langle \Delta_{\text{dp}}E_{\text{wBi}} \rangle_0$ 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. $\langle \Delta_{\text{dp}}E_{\text{H}_\text{O}^+} \rangle_0$ is calculated by vertical detachment of the extra adsorbed proton, and $\langle \Delta_{\text{dp}}E_{\text{wBi}} \rangle_0$ 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 recalculated at fixed atoms for each configuration.

$\langle \Delta_{\text{dp}}E_{\text{H}_\text{O}^+} \rangle_1$ and $\langle \Delta_{\text{dp}}E_{\text{wBi}} \rangle_1$ represent the energies associated to 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

the 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 $\langle \Delta_{\text{dp}} E_{\text{H}_\text{O}^+} \rangle_1$ a proton is added close to an O site in structural configurations of the neutral semiconductor-water interface, while the calculation of $\langle \Delta_{\text{dp}} E_{\text{wBi}} \rangle_1$ implies the insertion of a proton close to the adsorbed hydroxyl ion. For solutes in 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 a H^+ and a OH^- ^{31,40}) in two different positions within the supercell is subject to inaccuracies,³¹ even if this procedure preserves the charge neutrality of the supercell.

The energy of zero-point motion associated to protons for both solutes in aqueous solution and adsorbates are 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 H_2O molecule adsorbed on a Bi site for $\Delta_{\text{zp}} E_{\text{wBi}}$. 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 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}

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. Fig. 1), zero-point energies $\Delta_{\text{zp}}E$, and $\text{p}K_{\text{a}}$, 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, i.e. a difference of 0.4 units in the calculated $\text{p}K_{\text{a}}$ values. The $\text{p}K_{\text{a}}$ 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 $\text{BiVO}_4(010)$ in neutral conditions. In contrast, a water molecule adsorbed on the BiVO_4 surface results in a calculated $\text{p}K_{\text{a}}$ of 8.2, sensitively increased with respect to the acidity of a water molecule in the bulk liquid ($\text{p}K_{\text{a}}=15.74$). The bond between the Bi^{3+} site and the O atom of the water molecules allows for a partial transfer of positive charge to the latter, which, in turn, becomes more acidic, thus favouring 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 the quantities are recalculated at the hybrid functional level, we achieve $\text{p}K_{\text{a}}$ 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. 40 and 34. We calculate the pH_{PZC} of $\text{BiVO}_4(010)$ 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 $\text{p}K_{\text{a}}$ values, we infer that the dissociation of water molecules at the $\text{BiVO}_4(010)$ surface is clearly an unfavourable process. In fact, from Eq. (55) we calculate $\Delta A_{\text{d}}(\text{w}_{\text{M}}) = 0.72$ eV (0.73 eV at the h-rVV10 level of theory). This is consistent with the low reactivity and hydrophobicity of the surface.

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, H_O^+ , and for a water molecule adsorbed on a Bi site, w_{Bi} . Calculated 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.

		$\Delta\Delta_{\text{dp}}A$	$\Delta_{\text{zp}}E$	pK_a
H_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
$\text{H}_3\text{O}^+(\text{aq})$	r		0.32	-1.74
	h		0.34	-1.74

Our microscopic characterization of the acid-base chemistry at the different surface sites enables us to describe the pH-dependent interfacial coverage of the $\text{BiVO}_4(010)$ surface in 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 aqueous solution. We first calculate the surface concentration of Bi and O surface sites at the $\text{BiVO}_4(010)$ surface, which are 6.28×10^{-9} and 1.26×10^{-8} mol/dm², respectively. Next, we employ the definition of K_a :

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

and

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

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

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

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

subject to the conditions given by:

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

and

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

The diagram presented in Fig. 5 provides a rapid evaluation of the microstructural properties of the surface as 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 is at about three order of magnitude smaller than that of molecularly adsorbed water molecules. In fact, protons are found to be present in 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 favourable, 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 in order 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 favourable

mechanism occurring under basic conditions (i.e. the oxidation of the adsorbed hydroxyl ion⁶⁷). However, transition metal oxides in strong alkaline aqueous environment can undergo corrosion, thus undermining the stability of the device.⁵⁹

A partial hydroxylation of the BiVO₄ surface in near-neutral conditions has been recently detected by X-ray ambient pressure photoelectron spectroscopy studies of the BiVO₄-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 Fig. 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 on 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.

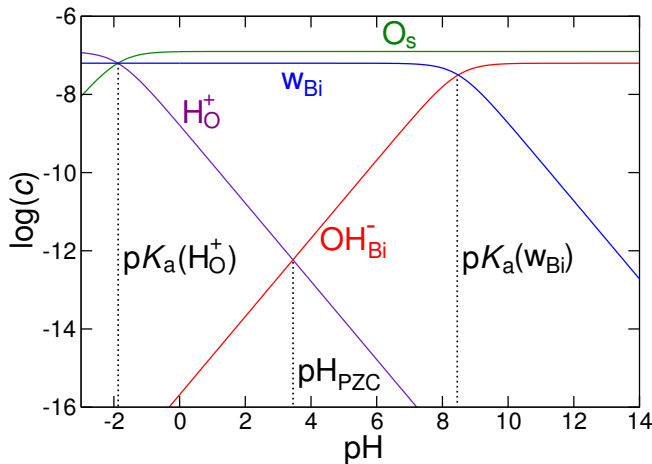


Figure 5: Acid-base logarithmic diagram for the coverage of the pristine BiVO₄(010) surface in aqueous environment, as calculated at the h-rVV10 level of theory. Concentrations are given in mol/dm².

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 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 (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 $\text{p}K_{\text{a}}$ 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 $\text{p}K_{\text{a}}$ values of the individual sites, we achieved a pH_{PZC} in excellent agreement with the experimental characterization. Furthermore, from the calculated $\text{p}K_{\text{a}}$ of the individual adsorption sites, we constructed an *ab initio* concentration diagram of all the 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 in order 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.

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Graphical TOC Entry

