

Water molecule adsorption properties on surfaces of MVO_4 ($M = \text{In, Y, Bi}$) photo-catalysts

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Abstract Water molecule adsorption properties at the surface of InVO_4 , YVO_4 , and BiVO_4 , which have indicated promising photocatalytic properties, have been investigated using an ab initio molecular dynamics approach. It was found that the water molecules were adsorbed dissociatively to the three-fold oxygen coordinated V (3c-V) sites on the (001) surface and 4c-In sites on the (100) surface of InVO_4 , however, in a non-dissociated molecular form on the 5c-Bi site on the (100) surface of BiVO_4 and the 7c-Y site on the (010) surface of YVO_4 . The adsorption energies of water molecule and geometries of the systems with adsorbed water molecules are reported in detail.

Keywords Photo-catalyst · Water molecule · Adsorption · First-principles molecular dynamics · YVO_4 · InVO_4 · BiVO_4 · TiO_2

1 Introduction

A photo-catalyst able to promote the decomposition of water molecules and operating in the frequency range of visible light (or in a wider wavelength region) is a primary

target in solar energy storage technology. Previously, we reported some preliminary experimental results concerning InVO_4 and YVO_4 which displayed a promising photocatalytic activity [1, 2]. In fact, hydrogen evolution could be observed in the visible range (from ultra violet (UV) region to 600 nm) in InVO_4 [1] and surprisingly high efficiencies in both O_2 and H_2 productions were achieved in YVO_4 system [2]. However, these two compounds still suffer from drawbacks. Namely, (1) The InVO_4 cannot produce O_2 and (2) the activity of YVO_4 is still limited to the UV region (<420 nm). On the other hand, it has been acknowledged that BiVO_4 shows some visible range response, however, it produces only oxygen in the presence of electron acceptors, like Ag^+ , provided by a *sacrificial* reagent like AgNO_3 and O_2 generation from pure water has not yet been observed [3, 4]. Ideally, both H_2 and O_2 evolutions are desirable and in principle it should be possible to obtain them in the visible range and in the near infra red up to wavelengths of about 1 μm (1.2 eV). In this work, to gain insight into the origin of the photo-catalytic activities of those interesting photocatalysts from a microscopic point of view, we have investigated the adsorption properties of H_2O molecules on the surface of InVO_4 , YVO_4 , and BiVO_4 by first principles molecular dynamics, within the Car–Parrinello scheme (CPMD) [5].

2 Structural properties of the crystals

Schematic crystal structures of those materials and rutile TiO_2 that is a well known photocatalyst are shown in Fig. 1 using polyhedral representation. The crystal structure parameters of InVO_4 , YVO_4 , and BiVO_4 are described in detail also in [6,7] and [8] respectively. The structural

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properties peculiar to each crystal can be summarized as follows:

2.1 InVO₄

The In site is surrounded by six oxygen atoms located at the corners of six different VO₄ tetrahedra (four-fold coordinated V; hereinafter called 4c-V). The In–O distances of the InO₆ octahedra (6c-In) are almost identical at about 2.16 Å. Each VO₄ tetrahedron is isolated and not linked to other VO₄ tetrahedra. Therefore, the V–V distance is large (4.05 Å). The characteristic V–O distance is 1.66–1.79 Å. The shortest O–O distance is ~2.7 Å and the In–In distance is 3.3 Å whereas the In–V distance is ~3.5 Å. The conduction band bottom of bulk InVO₄ is spanned by mainly V_3d atomic orbitals (~59%) and In_5s atomic orbitals (~19%), and the top of the valence band is composed of O_2p (~81%) [9]. The large contribution of In_5s components in the conduction band bottom is the specific feature of this catalyst system and may compensate for the low mobility of the electrons due to the large V–V distance. According to the electronic structure, the reduction should occur near the V or In site.

2.2 YVO₄

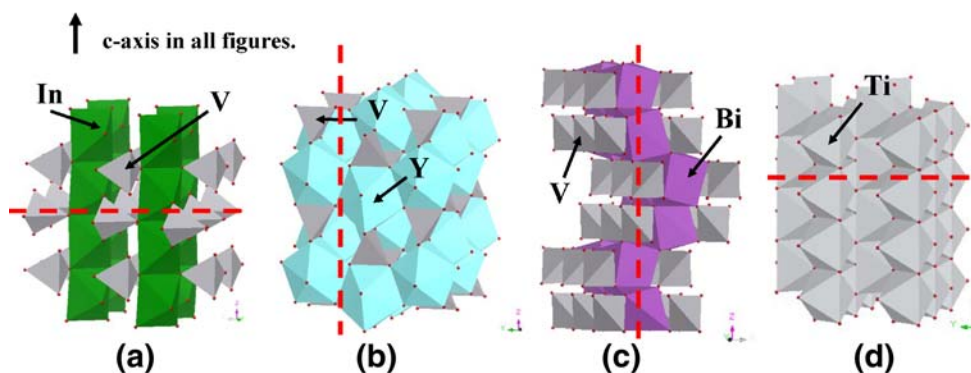
The YVO₄ crystal is formed by two kinds of polyhedra, a VO₄ tetrahedron and a YO₈ polyhedron. Each V is surrounded by four oxygen atoms with an atomic distance of 1.71 Å between the V and the O, and each Y is surrounded by eight oxygen atoms with a Y–O distance of either 2.29 Å (for four of eight Y–O bonds) or 2.44 Å (for other Y–O bonds). The shortest V–O distance is 1.7 Å and that of Y–O is about 2.3 Å. The shortest V–V, Y–Y, O–O, and V–Y distances are about 3.9 Å, 3.9 Å, 2.6 Å and 3.1 Å, respectively. This YVO₄ crystal structure is characterized by the fact that every VO₄ tetrahedron (YO₈ polyhedron) is isolated by a YO₈ polyhedron (VO₄ tetrahedron). These characteristics—each V forms VO₄ tetrahedron and the V–V distance is very large—are also found in the InVO₄ crystal. However, the YVO₄ crystal structure is quite different from

that of the InVO₄ crystal since the InVO₄ crystal has a laminated structure. The conduction band bottom of bulk YVO₄ is spanned by mainly V_3d atomic orbitals (~73%) and Y_4d atomic orbitals (~8%), and the top of the valence band is composed of O_2p (~83%). Therefore, the reduction should occur mainly at around the V site.

2.3 BiVO₄

The BiVO₄ compound has some different polymorphs. In our particular case, we selected the distorted sheelite structure (monoclinic), since its photo-catalytic activity has been shown to be higher than (at least) a tetragonal BiVO₄ [3, 4]. The V site in the BiVO₄ system is surrounded by four oxygen atoms forming a VO₄ tetrahedron (4c-V) and the typical V–O distance is 1.86–1.87 Å. Each VO₄ tetrahedron does not make contact with a subsequent VO₄ tetrahedron and the Bi site is surrounded by eight oxygen atoms (8c-Bi) which are located at the corners of eight different VO₄ tetrahedra [Fig. 1(c)], with Bi–O distances of 2.3–2.6 Å. The V–V distances in BiVO₄ are 3.9 Å and the shortest O–O distance is 2.6 Å. The Bi atoms can be ideally connected by segments of about 3.9 Å forming a continuous zigzag line along the (100) or (010) plane. The Bi–V distance is approximately 3.6–3.9 Å. The electronic structure of bulk BiVO₄ can be summarized as a conduction band bottom spanned mainly by V_3d atomic orbital (~79%) and a valence band top composed of O_2p (~64%) and Bi_6s (~18%) [9]. A remarkable feature is the large contribution of Bi_6s component to the valence band top. The presence of Bi atom could compensate, to some extent, the disadvantage in realizing high hole mobility due to the relatively large O–O separation (cf. 2.53 Å (rutile) and 2.45 Å (anatase) in TiO₂), then, oxidation process might be promoted. On the other hand, the V–V distances of BiVO₄ (3.9 Å) are considerably larger if compared with the Ti–Ti separation in the TiO₂ rutile and anatase, i.e. 2.96 Å and 3.04 Å, respectively [10, 11]. Since the connectivity of atomic wave functions which forms the conduction band is not good very much in this system, large electron mobility could not be expected and this thing

Fig. 1 Crystal structures of (a) InVO₄, (b) YVO₄, (c) monoclinic BiVO₄, and (d) rutile TiO₂ indicated with polyhedra representation, respectively. Red broken lines indicate cleavage surfaces using in the simulations



might be a disadvantage to realizing a high efficiency in reduction process.

3 Computational details

First-principles dynamic simulations were performed within the CPMD [5] using a Becke–Lee–Yang–Parr gradient corrected approach [12, 13]. The valence–core interaction was taken into account via norm-conserving Troullier–Martins pseudopotentials [14] for V, In, Y, Bi, and O atoms. For H, a Car-von Barth pseudopotential were used. In the case of V and Y, the use of semi-core states was needed in order to obtain a good description of both the geometry and the energetics. For In, and Bi, non-linear core correction was included. The electrons of V 3s, 3p, 3d, 4s; In 5s, 5p; Y 4s, 4p, 4d, 5s; Bi 5d, 6s, 6p; O 2s, 2p; H 1s were included in the valence electrons. Valence wave functions were expanded in plane waves with an energy cut-off of 80 Ry. A fictitious electronic mass of 1,200 a.u. and an integration step of 5.0 a.u. ensured a good control of the conserved quantities. The surface was represented by a slab using super cell, whose bottom layers were kept fixed to the bulk crystal, while the rest of the structure was fully relaxed. An empty space whose thickness is more than 10 Å was prepared above the relaxed crystal surface in every case to keep the system far from its repeated images since periodic boundary conditions are imposed. Stoichiometric, non-charged systems were employed in all cases. We started by considering the dynamical properties of water molecule adsorption using CPMD by placing water molecules with setting the distances at ~3 Å or more above the catalyst surface in initial starting configurations. The temperature was controlled by a velocity rescaling algorithm at 300 K within an error bar of 10~15 K. After the system reached thermal equilibrium state, a full static relaxation was performed to obtain the adsorption energy per single water molecule. More detailed information on the super cell used in each case is as follows:

3.1 InVO₄

To study the water molecule adsorption property of the V adsorption site, the (001) surface of InVO₄, where both O and V atoms are exposed, was prepared. In case of the (001) surface, the exposed V site is surrounded by three oxygen atoms (three-fold coordinated V; hereinafter 3c-V) and the In site close to the top surface is surrounded by six oxygen atoms (6c-In). The super cell includes two unit cells of InVO₄ corresponding to a size of 2a×b×c. The super cell size is 2a×b×(c+empty space)=11.53×8.542×(6.592+9.898) Å³ (=1.62 nm³) and the size of simulated surface, which is obtained by cleaving at the broken line in Fig. 1(a),

is 2a×b=98.5 Å², which is roughly identical to the size of one mono-molecular H₂O layer including ten H₂O molecules (10×3.1²=96.1 Å²) in room condition (P=1 atm, T=298 K). The super-cell has eight In, eight V, and 32 O atoms plus one H₂O molecule.

On the other hand, the water molecule adsorption properties of the In site were investigated by using the (100) surface, where the exposed In site is surrounded by four oxygen atoms (4c-In) and the V site close to the top surface is fourfold coordinated (4c-V). The super cell includes four unit cells of InVO₄ corresponding to a size of 2a×b×2c. The super cell size is (2a+empty space)×b×2c=(11.53+11)×8.542×13.184 Å³ (=2.54 nm³) and the size of simulated surface, which is obtained by cleaving at the broken line in Fig. 3(a), is b×2c=112.6 Å², which is roughly identical to the size of one mono-molecular H₂O layer including 11.7 H₂O molecules in room condition. The super-cell has 16 In, 16 V, and 64 O atoms plus 12 or 2 H₂O molecules.

3.2 YVO₄

In the present study we focus on the (010) surface, where both O and Y atoms are exposed. We examined the surface in the presence of one H₂O molecule. The exposed Y site is surrounded by seven oxygen atoms (7c-Y) and the V site close to the top surface forms 4c-V. The super cell contains four unit cells of YVO₄ corresponding to a size of 2a×a×2c. The super cell size is 2a×(a+empty space)×2c=14.2312 Å×(7.1156+11.3850) Å×12.5740 Å (=3.31 nm³) and the size of simulated surface, which is obtained by cleaving at the broken line in Fig. 1(b), is 2a×2c=178.94 Å², which is roughly identical to the size of one mono-molecular H₂O layer including 18.6 H₂O molecules in room condition. The super-cell has 16 Y, 16 V, and 64 O atoms plus one H₂O molecules.

3.3 BiVO₄

In the present study we focus on the (100) surface, where both O and Bi atoms are exposed. We examined the surface in the presence of one H₂O molecule [15¹]. The exposed Bi site is surrounded by five oxygen atoms (5c-Bi) and the V site close to the top surface is 4c-V. The simulated system consists of two unit cells of BiVO₄ corresponding to a global size of a×2b×c. For simplification, we have approximated the β angle to 90°, which is however very close to the reported experimental value (90.43°) [16]. The super cell size is (a+empty space)×2b×c=(5.186+

¹ The Figs. 5 (a) and (b) are obtained by refining the Fig. 4 (a) of reference 15 by making the system reach thermal equilibrium state at 300 K before the geometry optimization.

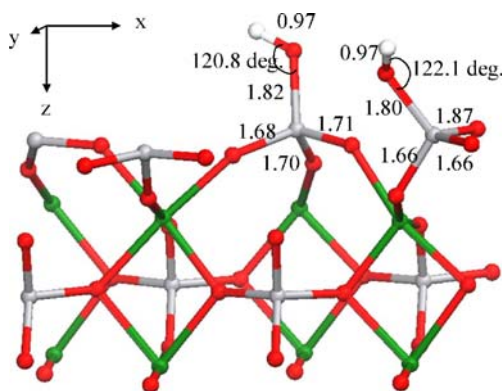


Fig. 2 Schematic representation from (010) direction of the geometry of the InVO_4 slab system with one dissociated water molecule on the surface after geometry optimization and 1.1 ps constant temperature dynamics at 300 K. In, V, O and H atoms are indicated in green, gray, red and white balls, respectively. Each atomic distance is shown in Å unit

13.335) Å \times 10.200 Å \times 11.708 Å (=2.2 nm³) and the simulated surface size, which is obtained by cleaving at the broken line in Fig. 1(c), is $2b \times c = 119$ Å² corresponding to the size of one mono-molecular H_2O layer by 12.4 H_2O molecules. The super-cell has eight Bi, eight V, and 32 O atoms plus one H_2O molecules.

4 Results and discussions

4.1 InVO_4

Firstly, the dynamic features of the system with a single water molecule placed near the (001) surface of InVO_4 at 300 K were investigated. During the dynamics, whenever a water

molecule approaches the exposed V atoms of 3c-V structures of the (001) surface, a strong interaction occurs between V and the lone pair of electrons of the O atom of the H_2O molecule. Not only is the O_{water} atom attracted by the $\text{V}_{\text{surface}}$ but the H_{water} atoms are also often drawn to the $\text{O}_{\text{surface}}$ atoms to form hydrogen bonds. When the water molecule was firmly captured in this way by the $\text{V}_{\text{surface}}$ and $\text{O}_{\text{surface}}$, the H_2O molecule was spontaneously dissociated. At the moment the water molecule dissociated, the distance between the O_{water} and the $\text{V}_{\text{surface}}$ was about 1.9 Å. (This is almost same as the case of 4c-Ti formed in a rutile TiO_2 (001) surface cleaved by the broken line in Fig. 1 (d). The Ti– O_{water} distance when the water molecule dissociates is about 2.0 Å.) After investigating the dynamics for 1.1 ps, we optimized the geometry of the system to investigate the structural properties of adsorbate and adsorption energy by performing a full relaxation until the residual forces were less than 10 meV/Å (Fig. 2). It was found that the separated hydroxyl–O–H from the water molecule was bound to 3c-V forming VO_4 tetrahedral structure and the other hydrogen atom was bound to $\text{O}_{\text{surface}}$. The V–O equilibrium distances of the VO_4 are 1.68 Å~1.82 Å. The estimated dissociative absorption energy of H_2O to the 3c-V site was ~0.8 eV per molecule.

On the other hand, during the dynamics in case of the (100) surface which includes the exposed In atoms of 4c-In, a strong interaction occurs between the exposed In atoms on the surface and the lone pair of electrons of the O atom of the H_2O molecule. Not only is the O_{water} atom attracted by the $\text{In}_{\text{surface}}$ but also the H_{water} atoms of the water molecule adsorbed to In site are often drawn to the O_{water} atoms of other water molecule to form hydrogen bonds. When the water molecule was firmly captured by the In and attracted

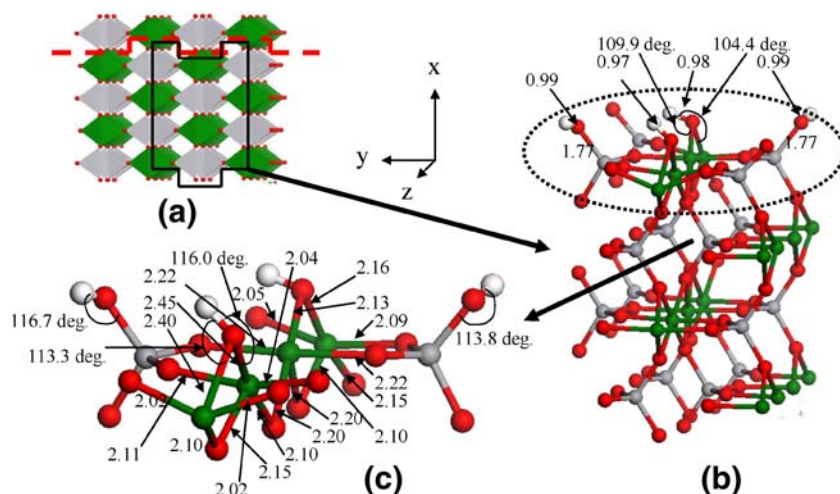
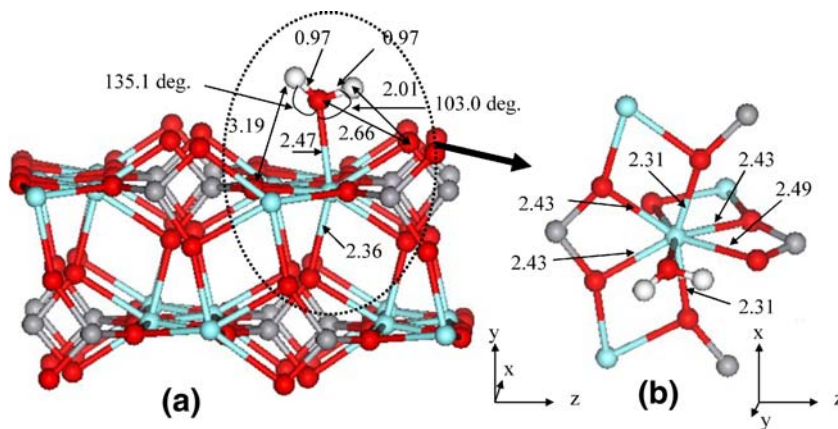


Fig. 3 (a) The view from direction tilted a little from (001) direction of InVO_4 crystal indicated with polyhedra representation. Red broken line indicates a cleavage surface using in the simulations with respect to the surface exposing 4c-In. (b) Schematic representation, from direction as same as in case of (a), of the geometry of the InVO_4 slab

system with two dissociated H_2O molecules on the surface obtained after geometry optimization following the process described in the text. (c) More detailed adsorbate structures. Atoms and atomic distances are indicated using the same colors and unit as in the Fig. 2

Fig. 4 (a) View of the geometry of the YVO_4 slab system, from $(\bar{1}00)$ direction, with one H_2O molecule on the surface as obtained after geometry optimization. (b) More detailed adsorbate structures from $(0\bar{1}0)$ direction. Y atoms are indicated in *sky blue* and atomic distances and other atoms are indicated using same unit and colors as in the Fig. 2



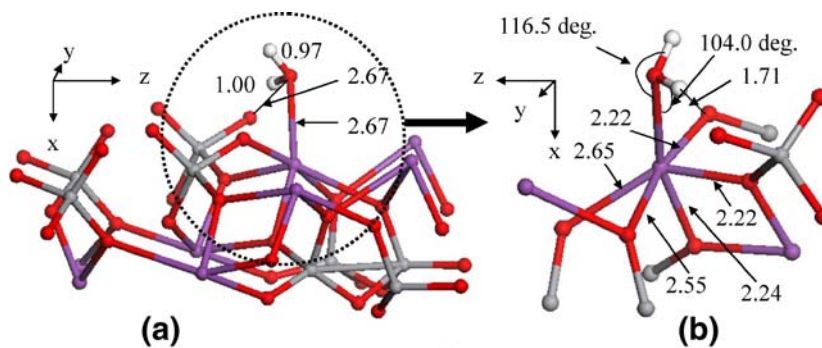
by the other H_2O molecule in this way, the H_2O molecule was spontaneously dissociated. At the moment the water molecule dissociated, the distance between the O_{water} and the $\text{In}_{\text{surface}}$ was about $2.2\text{--}2.3$ Å and that between the O_{water} of water molecule adsorbed to the substrate and the O_{water} of water molecule moving around the adsorbate was about $2.4\text{--}2.5$ Å. After investigating the dynamics for 3.1 ps, we removed ten water molecules from the super cell leaving the dissociated two water molecules on the surface in order to exclude the energy contributions coming from complicated hydrogen binding at the stage of water cluster formation and then the geometry of the system was optimized to estimate the water molecule adsorption energy until the residual forces were less than 50 meV/Å [Fig. 3 (b) and (c)]. It was found that the separated hydroxyl–O–H from the water molecule was bound to 4c-In forming InO_5 structure and the other hydrogen atom was bound to $\text{O}_{\text{surface}}$ atoms which are coordinated with V atoms. The $\text{In}\text{--}\text{O}_{\text{water}}$ equilibrium distances are approximately 2.1 Å \sim 2.4 Å. The estimated dissociative absorption energy of H_2O to the 4c-In site was ~ 1.9 eV per molecule in average.

4.2 YVO_4

During the dynamics at thermal equilibrium state at 300 K, we noticed that the lone pairs of the O atom of the H_2O

molecule interacted with the exposed 7c-Y atom of the (010) surface and water molecule tends to stay close to the 7c-Y site keeping the $\text{Y}\text{--}\text{O}_{\text{water}}$ distance at $2.35\text{--}2.88$ Å in a stable water adsorption (average) configuration. Being different from the former cases, no spontaneous dissociative adsorption could be found. Furthermore water molecules are never adsorbed directly at exposed 4c-V sites, but we could see the formation of hydrogen bonds between the H_{water} and $\text{O}_{\text{surface}}$ atom which is shared by the 4c-V and the 7c-Y polyhedra. After observing the thermal equilibrium state, the system was optimized with the full relaxation until the residual forces were less than 10 meV/Å. Figure 4 shows the geometry of this single H_2O adsorption on the (010) YVO_4 surface, adsorbed in a non-dissociated form. The Y adsorption site becomes eightfold coordinated. The $\text{Y}\text{--}\text{O}_{\text{water}}$ distances is 2.47 Å. The other distances of the $\text{Y}\text{--}\text{O}_{\text{surface}}$ bonds are 2.47 Å, 2.49 Å, 2.43 Å, 2.36 Å, 2.43 Å, 2.31 Å, and 2.31 Å, respectively. They are not much different from the typical $\text{Y}\text{--}\text{O}$ bond of the bulk crystal ($2.29\text{--}2.44$ Å; 2.37 Å, in average) where a shell of eight O atoms surrounds Y. Furthermore, the hydrogen atom belonging to the water molecule is drawn to the surface oxygen of YVO_4 . The equilibrium distance between H_{water} and $\text{O}_{\text{surface}}$ is 2.10 Å and the separation between O_{water} and $\text{O}_{\text{surface}}$ is 2.66 Å. The absorption energy of H_2O to Y is estimated to be ~ 0.64 eV per molecule.

Fig. 5 (a) View of the geometry of the BiVO_4 slab system, from $(0\bar{1}0)$ direction, with one H_2O molecule on the surface as obtained after geometry optimization. (b) More detailed adsorbate structures from the other direction. Bi atoms are indicated in *purple* and atomic distances and other atoms are indicated using the same unit and colors as in the Fig. 2



4.3 BiVO₄

During the dynamics, we noticed that whenever a water molecule comes in proximity of the (100) surface exposing 5c-Bi atoms, a strong interaction occurs between Bi and the lone pairs of the O atom of the H₂O molecule. However, even in the case of the closest approach of an O_{water} atom to a 5c-Bi site, 2.44 Å, we did not observe any spontaneous dissociation of the water molecule. Moreover, water molecules are never adsorbed directly at exposed 4c-V sites, but we could see the formation of hydrogen bonds between O atom coordinated to the V atom and the H_{water} atom as seen in the case of YVO₄. After reaching thermal equilibrium, the full relaxation was performed to obtain the adsorption energy per single water molecule. It was performed until the residual forces were less than 10 meV/Å. Figure 5 shows the geometry of this single H₂O adsorption on the (100) BiVO₄ surface, adsorbed in a non-dissociated form. The bismuth atom at the surface is now surrounded by six oxygen atoms due to the water molecule adsorption. The Bi–O equilibrium distances are 2.24 Å, 2.22 Å, 2.22 Å, 2.55 Å, 2.65 Å and 2.67 Å, respectively. They are not much different from the typical Bi–O bond of the bulk crystal (2.3–2.6 Å; 2.43 Å, in average) where a shell of eight O atoms surrounds Bi. The equilibrium bond distance of H_{water} and O_{surface} by hydrogen bonding is 1.71 Å, and the separation between the O_{water} and the O_{surface} is 2.67 Å. The estimated absorption energy of H₂O to 5c-Bi turns out to be ~0.58 eV per molecule.

5 Summary

Throughout this study, we have found a tendency that if oxygen atoms of water molecules can come in proximity of the exposing cation atoms on the catalyst surface at a

distance of less than 2.3 Å, the water molecules are spontaneously dissociated at room temperature. Although the adsorption only describes the first step in the complex photo catalysis process that, after the dissociative adsorption, electrons and holes have to do their reducing and oxidizing work and then the reaction products have to be desorbed, it would be important as a necessary condition for developing a photocatalyst with a higher performance that the system be designed to produce short water-catalyst distances and imperfectly oxygen coordinated cation sites be on the catalyst surface in a stable state.

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