

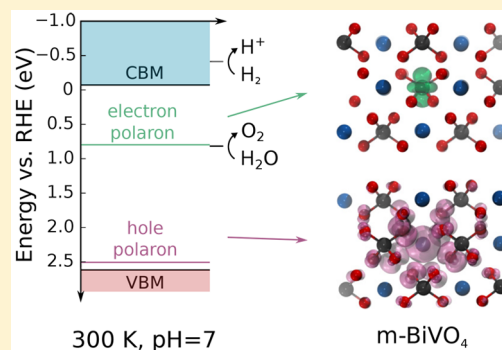
Role of Polarons in Water Splitting: The Case of BiVO₄

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S Supporting Information

ABSTRACT: We study hole and electron polarons in BiVO₄ at finite temperature through hybrid functional molecular dynamics simulations. Through the thermodynamic integration method, we obtain the transition levels corresponding to the localized charges at 300 K. We observe that the polaron levels achieved in this way lie significantly closer to each other than those at 0 K. We find both hole and electron levels to lie within the band gap, with binding energies of 0.11 and 0.88 eV, respectively. Our calculations show that polaron localization significantly affects the alignment at the solid/liquid interface and that electron–hole recombination through polaronic states competes with the evolution of the water-splitting reaction in BiVO₄.



Photocatalytic water splitting is a promising way of generating chemical fuels from solar energy.^{1–3} To achieve higher efficiency of photoelectrochemical cells, the search for new functional materials with optimal properties is ongoing. Several high-throughput studies have recently been undertaken and resulted in the proposal of several ternary metal oxide semiconductors as suitable absorber candidates.^{4–7} Because these findings inspire considerable experimental effort, it is of great importance to verify the usefulness of the considered descriptors. In the computational screening of photoabsorbers for water splitting, two requirements are generally considered. First, the band gap of the semiconductor has to be larger than at least 1.23 eV, which is the energy per transferred electron needed to split water. Accounting for losses at the semiconductor–liquid junction due to, e.g., overpotentials, the minimal value should rather be 1.6–2.4 eV.^{8,9} Second, for single-absorber photoelectrochemical devices, the redox potentials of water should be straddled by the valence band maximum (VBM) and conduction band minimum (CBM) of the semiconductor.^{3,10} This is based on the assumption that the H⁺ reduction and H₂O oxidation are driven by delocalized holes and electrons occupying the highest and lowest levels of the valence and conduction bands, respectively.

It has been shown for many metal oxides that excess charges induce lattice distortion and form localized polarons.^{11–17} If stable, such quasiparticles occupy energy levels within the gap. Therefore, upon their creation within the semiconductor, the charge carriers diffuse through the lattice by hopping from one stable position to another until they recombine, get trapped, or reach the solid/liquid interface. Besides inhibiting carrier

transport kinetics, the formation of polarons might also impact the catalysis process at the interface. Because the water-splitting reaction is driven by photogenerated excess charges, the reaction can only occur if the redox levels are straddled not only by the band edges but also by the polaron levels. This is in contrast with the previously described screening methodologies for metal oxide photoabsorbers and might prove a crucial factor in future material discovery efforts.

Monoclinic bismuth vanadate (m-BiVO₄) has been considered a promising photoanode for water-splitting photoelectrochemical cells^{18–21} and has thus been extensively studied both experimentally and computationally. Because BiVO₄ is representative of a broader class of complex metal oxides,²² it can be used as a benchmark material to understand crucial phenomena affecting the water-splitting reaction. Additionally, polarons in BiVO₄ have already been observed.^{16,17,23–27} However, previous theoretical studies only considered charge localization at 0 K, while the electronic structure of BiVO₄ is strongly affected by thermal distortions.²⁸ Additionally, the thermodynamic transition levels of polarons in this material have not been addressed so far.

In this Letter, we highlight the effect of polaronic energy levels on water splitting by applying state-of-the-art computational methods. To achieve a realistic description of the localization of excess holes and electrons in BiVO₄, we perform hybrid functional molecular dynamics (MD) simulations. We determine the polaron binding energies at finite temperature

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through the thermodynamic integration method, which is suitable for calculating free-energy differences. Finally, we align the polaronic levels with the redox potentials of water and discuss the consequences of this alignment on the water-splitting reaction.

Because standard semilocal functionals are not able to treat the self-interaction error^{29–31} and erroneously favor the delocalization of electronic states, we study the polarons with the hybrid functional PBE0.³² We set the α parameter to 0.22 as this value leads to a fundamental band gap in agreement with experiment (about 2.6 eV), after including all relevant corrections.²⁸ The MD simulations are performed with the CP2K code³³ in the canonical NVT ensemble at a temperature of 300 K. The orbitals are described with atom-centered Gaussian-type basis functions, and the electron density is re-expanded with an auxiliary plane-wave basis set. We use the MOLOPT basis set³⁴ for Bi, O, and V and a cutoff of 600 Ha for the plane waves. Core–valence interactions are described by Goedecker–Teter–Hutter pseudopotentials.³⁵ The calculations are carried out for an optimized orthorhombic supercell containing 192 atoms ($a = 10.30$, $b = 10.26$, and $c = 23.50$ Å), and the Brillouin zone is sampled at the Γ point. The time step is set to 1 fs, and the simulations are carried out for 5–10 ps. We study hole and electron polarons by removing or adding one electron to the supercell. In this case, we perform spin-polarized calculations. Because the CP2K code does not include spin–orbit effects and only allows for Γ -point sampling of the Brillouin zone, we correct the positions of the band edges of BiVO₄ using the results of ref 28. We neglect finite-size corrections in the calculations³⁶ due to the high dielectric constant of BiVO₄ ($\epsilon_0 = 68$).³⁷

To obtain the energy levels of the hole and electron polarons, we follow the grand-canonical formulation for defects in crystalline materials.^{36,38} In this case, the charge transition level μ can be written as

$$\mu(q/q') = \frac{G^q[X] - G^{q'}[X]}{q' - q} - \epsilon_v \quad (1)$$

where $G^q[X]$ and $G^{q'}[X]$ are the free energies of the defect X in the charge states q and q' and ϵ_v is the position of the VBM. To take into account the thermal disorder, we calculate free-energy differences with the thermodynamic integration method.³⁹ In the following, we neglect volume changes and apply the linear Marcus approximation. The hole polaron level can then be calculated as⁴⁰

$$\mu(h_{\text{loc}}) = \frac{\langle \Delta E_h \rangle_0 + \langle \Delta E_h \rangle_1}{2} - \epsilon_v \quad (2)$$

where $\langle \Delta E_h \rangle_0$ is the energy of vertical removal of one electron in the bulk configuration and $\langle \Delta E_h \rangle_1$ is the energy of adding an electron in the geometry of the hole polaron. In the case of the electron, the transition level reads

$$\mu(e_{\text{loc}}) = \frac{\langle \Delta E_{\text{el}} \rangle_0 + \langle \Delta E_{\text{el}} \rangle_1}{2} - \epsilon_v \quad (3)$$

where $\langle \Delta E_{\text{el}} \rangle_0$ corresponds to the vertical injection of one electron in the bulk geometry and $\langle \Delta E_{\text{el}} \rangle_1$ to the removal of an electron in the polaron geometry. In the case of the electron, for which the energy differences are larger, we examine the validity of the linear Marcus approximation by including an additional value of the Kirkwood coupling parameter^{39,41} at

0.5. The additional point changes the position of the electron polaron transition level by only 0.07 eV.

First, we study the electron and hole polarons at 0 K. The charge localization is given in Figure 1. The charge distribution

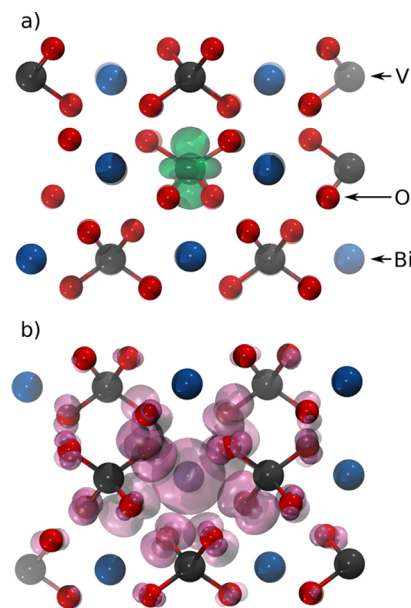


Figure 1. Isodensities of the (a) electron and (b) hole polarons in monoclinic BiVO₄ at 0 K. The electron is localized around a vanadium atom and the hole around a bismuth atom.

is consistent with previous studies.^{24,25} The electron polaron localizes around a vanadium atom, which changes its ionization state from +5 to +4. At the same time, the V–O bond lengths around the polaron increase, from about 1.72 to 1.81 Å. The localized polaron introduces a one-particle level within the band gap at 1.43 eV below the CBM. Through eq 1, we find that the associated transition level lies at 1.09 eV below the CBM.

The hole polaron is mostly distributed between one bismuth and eight oxygen atoms. The charge localization results in Bi–O bond shortening, from about 2.48 Å on average to about 2.42 Å. The charge occupies a one-particle level at 0.78 eV above the VBM. Through eq 1, we obtain a transition level at 0.30 eV above the VBM. We give the alignment of the polaronic transition levels with the band edges of BiVO₄ in Figure 2. We note that the fundamental (electronic) band gap at 0 K amounts to 3.61 eV when calculated with the current setup. This results in a band gap of 2.69 eV after including thermal and quantum renormalization effects.²⁸

In ref 28, we observed that the electronic structure of BiVO₄ is strongly affected by thermal disorder. We also expect the temperature to have an effect on the polaronic energy levels. Therefore, we determine the polaronic energy levels through thermodynamic integration based on hybrid functional molecular dynamics. First, we study the evolution of the electron polaron. We observe that during a MD duration of 5 ps the electron remains localized around the same vanadium atom. Also, the geometry around the V⁴⁺ ion does not change as the average V–O bond length still amounts to 1.81 Å. Through thermodynamic integration at 300 K, we obtain a transition level at 0.88 eV below the CBM, as illustrated in Figure 2. The binding energy of the electron polaron (energy separation from the CBM) reduces by 0.21 eV due to

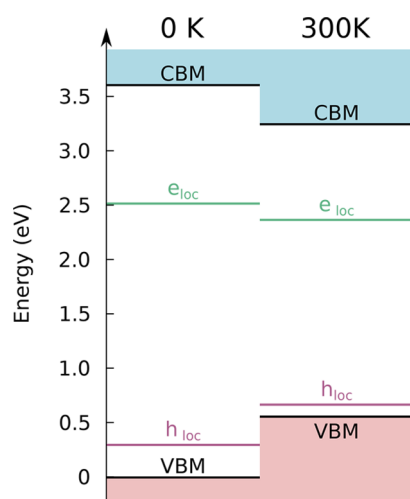


Figure 2. Energy diagram showing the transition levels of the hole and electron polarons with respect to the band edges of BiVO_4 at 0 and 300 K. The results are aligned through the V 3s level.

temperature, while the absolute position of the transition level shifts by 0.16 eV toward lower energies.

For the hole polaron, we carry out molecular dynamics lasting for 10 ps. Because the hole polaron is much less localized than the electron, we observe polaron hopping and the charge localizes around various bismuth atoms during the simulation. Most of the time, the charge is distributed between one bismuth and eight oxygen atoms. In about 20% of the configurations, we observe a stronger localization of the hole, mostly at a single oxygen atom. From the thermodynamic integration, we obtain a transition level lying at 0.11 eV above the VBM, consistent with the weaker charge localization compared to the electron polaron. We note that the calculated binding energy of the hole polaron at 300 K is close to the thermal hopping activation energy of about 0.09 eV, derived from THz spectroscopy measurements.¹⁶ The different localization of the hole and the electron polaron is consistent with the observation that the electron mobility limits the photocarrier transport and extraction in BiVO_4 .^{42–45} The relatively weak localization of the hole polaron is also in line with the study of Butler et al.,¹⁷ who observed that above a critical Mott concentration the wave function of trapped positive charges can overlap, leading to an enhanced charge mobility. We note that the binding energy of the hole at 300 K is lower than the one calculated at 0 K by 0.30 eV, similar to the case of the electron polaron. Further, we observe that at 300 K the polaronic energy levels also differ from the 0 K case on an absolute energy scale (see Figure 2).

Next, we consider the effect of the energy levels of the electron and hole polarons on the water-splitting reaction. First, we observe that the energy separation between the localized charge carriers amounts to 1.70 eV. This is smaller by about 1 eV than the fundamental band gap of 2.69 eV. This considerable difference shows how drastic of an effect the localization of charge carriers can have on the alignment of the energy levels in this class of materials. The significant difference between the energy levels of delocalized and localized states highlighted here could have a critical impact on the search for new materials among metal oxides.

In Figure 3 we align the band edges and the polaronic levels with the H^+/H_2 and $\text{H}_2\text{O}/\text{O}_2$ redox levels. The alignment of these levels is illustrated for pH = 7. For this purpose, we use

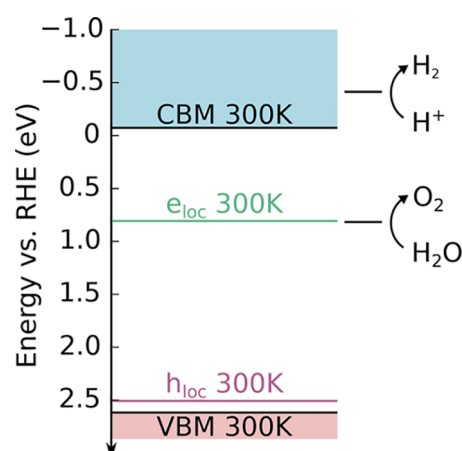


Figure 3. Alignment of the band edges of BiVO_4 and polaron transition levels at 300 K with H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ redox levels at pH = 7.

the pH of the zero-point charge of BiVO_4 calculated in ref 46 and the band alignment at the BiVO_4 /water interface given in ref 47. We note that, as the same pH dependence (Nernstian behavior) is expected for all presented levels, the relative positions of the various levels will be preserved at other pH.

The hole polaron in BiVO_4 is relatively weakly localized, and hence, the $\text{H}_2\text{O}/\text{O}_2$ redox level is positioned above both the VBM and the polaron level. However, the electron polaron level falls very close to the $\text{H}_2\text{O}/\text{O}_2$ redox level. This means that the recombination process between electron and hole polarons at the BiVO_4 /water interface could compete with charge transfer to the electrolyte. This observation is in agreement with experimental findings showing that the photocurrent of BiVO_4 is limited by surface recombination processes.⁴⁸ We note that the binding energies of the polarons are expected to increase near the surface, which would imply an even stronger tendency toward recombination.

Polaron levels as calculated in the present work would also severely restrict the scope of band level engineering efforts. The H^+/H_2 potential is found at 0.34 eV above the CBM, which suggests that the band edge could reach this level through band structure engineering and that slightly modified monoclinic BiVO_4 could be suitable for driving overall water splitting. However, considering that the localized electron lies at 1.22 eV below the redox potential, water reduction would be much more difficult to achieve. This is consistent with the fact that the overall water-splitting reaction based on BiVO_4 could only be achieved through strong modification of its structure or composition by alloying.^{49,50} The points mentioned above suggest that a reevaluation of the descriptors used in materials screening processes might be in order to account for charge localization in metal oxides.

In conclusion, we highlighted the role of hole and electron polarons in BiVO_4 at finite temperature by combining the thermodynamic integration method and hybrid functional molecular dynamics simulations. The polaron levels calculated at 300 K lie significantly closer to each other than those at 0 K. We found that localization of both the hole and the electron introduces levels within the band gap, with binding energies of 0.11 and 0.88 eV, respectively. The polaron localization significantly affects the alignment at the BiVO_4 /water interface, suggesting that electron–hole recombination through polar-

onic states could hamper the evolution of the water-splitting reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b00938.

Sample CP2K input file used to study the electron polaron in BiVO₄ at 0 K (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.
- (2) Maeda, K.; Teramura, K.; Lu, D.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. Photocatalyst Releasing Hydrogen from Water. *Nature* **2006**, *440*, 295–295.
- (3) 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.
- (4) 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.
- (5) 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.
- (6) Zhou, L.; Yan, Q.; Shinde, A.; Guevarra, D.; Newhouse, P. F.; Becerra-Stasiewicz, N.; Chatman, S. M.; Haber, J. A.; Neaton, J. B.; Gregoire, J. M. High Throughput Discovery of Solar Fuels Photoanodes in the CuO–V₂O₅ System. *Adv. Energy Mater.* **2015**, *5*, 1500968.
- (7) Yan, Q.; Yu, J.; Suram, S. K.; Zhou, L.; Shinde, A.; Newhouse, P. F.; Chen, W.; Li, G.; Persson, K. A.; Gregoire, J. M.; et al. Solar Fuels Photoanode Materials Discovery by Integrating High-Throughput Theory and Experiment. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 3040–3043.
- (8) Bolton, J. R.; Strickler, S. J.; Connolly, J. S. Limiting and Realizable Efficiencies of Solar Photolysis of Water. *Nature* **1985**, *316*, 495–500.
- (9) Turner, J. A. A. Realizable Renewable Energy Future. *Science* **1999**, *285*, 687–689.
- (10) Nørskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. Towards the Computational Design of Solid Catalysts. *Nat. Chem.* **2009**, *1*, 37.
- (11) Di Valentin, C.; Selloni, A. Bulk and Surface Polarons in Photoexcited Anatase TiO₂. *J. Phys. Chem. Lett.* **2011**, *2*, 2223.
- (12) Setvin, M.; Franchini, C.; Hao, X.; Schmid, M.; Janotti, A.; Kaltak, M.; Van de Walle, C. G.; Kresse, G.; Diebold, U. Direct View at Excess Electrons in TiO₂ Rutile and Anatase. *Phys. Rev. Lett.* **2014**, *113*, 086402.
- (13) Janotti, A.; Varley, J. B.; Choi, M.; Van de Walle, C. G. Vacancies and Small Polarons in SrTiO₃. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *90*, 085202.
- (14) Bjaalie, L.; Janotti, A.; Krishnaswamy, K.; Van de Walle, C. G. Point Defects, Impurities, and Small Hole Polarons in GdTiO₃. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 115316.
- (15) Rettie, A. J.; Chemelewski, W. D.; Emin, D.; Mullins, C. B. Unravelling Small-Polaron Transport in Metal Oxide Photoelectrodes. *J. Phys. Chem. Lett.* **2016**, *7*, 471–479.
- (16) Ziwrtsch, M.; Müller, S.; Hempel, H.; Unold, T.; Abdi, F. F.; van de Krol, R.; Friedrich, D.; Eichberger, R. Direct Time-Resolved Observation of Carrier Trapping and Polaron Conductivity in BiVO₄. *ACS Energy Lett.* **2016**, *1*, 888–894.
- (17) Butler, K.; Dringoli, B.; Zhou, L.; Rao, P.; Walsh, A.; Titova, L. Ultrafast Carrier Dynamics in BiVO₄ Thin Film Photoanode Material: Interplay Between Free Carriers, Trapped Carriers and Low-Frequency Lattice Vibrations. *J. Mater. Chem. A* **2016**, *4*, 18516–18523.
- (18) 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.
- (19) Yu, J.; Kudo, A. Effects of Structural Variation on the Photocatalytic Performance of Hydrothermally Synthesized BiVO₄. *Adv. Funct. Mater.* **2006**, *16*, 2163–2169.
- (20) Luo, H.; Mueller, A. H.; McCleskey, T. M.; Burrell, A. K.; Bauer, E.; Jia, Q. Structural and Photoelectrochemical Properties of BiVO₄ Thin Films. *J. Phys. Chem. C* **2008**, *112*, 6099–6102.
- (21) 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.
- (22) Sharp, I. D.; Cooper, J. K.; Toma, F. M.; Buonsanti, R. Bismuth Vanadate As a Platform for Accelerating Discovery and Development of Complex Transition-Metal Oxide Photoanodes. *ACS Energy Lett.* **2017**, *2*, 139–150.
- (23) Kweon, K. E.; Hwang, G. S. Surface Structure and Hole Localization in Bismuth Vanadate: A First Principles Study. *Appl. Phys. Lett.* **2013**, *103*, 131603.
- (24) Kweon, K. E.; Hwang, G. S. Structural Phase-Dependent Hole Localization and Transport in Bismuth Vanadate. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 205202.
- (25) Kweon, K. E.; Hwang, G. S.; Kim, J.; Kim, S.; Kim, S. Electron Small Polarons and Their Transport in Bismuth Vanadate: A First Principles Study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 256–260.
- (26) Liu, T.; Zhou, X.; Dupuis, M.; Li, C. The Nature of Photogenerated Charge Separation Among Different Crystal Facets of BiVO₄ Studied by Density Functional Theory. *Phys. Chem. Chem. Phys.* **2015**, *17*, 23503–23510.
- (27) Rettie, A. J.; Chemelewski, W. D.; Lindemuth, J.; McCloy, J. S.; Marshall, L. G.; Zhou, J.; Emin, D.; Mullins, C. B. Anisotropic Small-Polaron Hopping in W: BiVO₄ Single Crystals. *Appl. Phys. Lett.* **2015**, *106*, 022106.
- (28) Wiktor, J.; Reshetnyak, I.; Ambrosio, F.; Pasquarello, A. Comprehensive Modeling of the Band Gap and Absorption Spectrum of BiVO₄. *Phys. Rev. Mater.* **2017**, *1*, 022401.
- (29) Zhang, Y.; Yang, W. A Challenge for Density Functionals: Self-Interaction Error Increases for Systems with a Noninteger Number of Electrons. *J. Chem. Phys.* **1998**, *109*, 2604–2608.
- (30) Pacchioni, G.; Frigoli, F.; Ricci, D.; Weil, J. A. Theoretical Description of Hole Localization in a Quartz Al Center: The Importance of Exact Electron Exchange. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *63*, 054102.

- (31) Lægsgaard, J.; Stokbro, K. Hole Trapping at Al Impurities in Silica: A Challenge for Density Functional Theories. *Phys. Rev. Lett.* **2001**, *86*, 2834.
- (32) Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for Mixing Exact Exchange with Density Functional Approximations. *J. Chem. Phys.* **1996**, *105*, 9982–9985.
- (33) 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.
- (34) VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *J. Chem. Phys.* **2007**, *127*, 114105.
- (35) Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-Space Gaussian Pseudopotentials. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 1703–1710.
- (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) Wee, S.-H.; Kim, D.-W.; Yoo, S.-I. Microwave Dielectric Properties of Low-Fired ZnNb_2O_6 Ceramics with BiVO_4 Addition. *J. Am. Ceram. Soc.* **2004**, *87*, 871–874.
- (38) 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.
- (39) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Academic Press: San Diego, CA, 2002.
- (40) Ambrosio, F.; Wiktor, J.; De Angelis, F.; Pasquarello, A. Origin of Low Electron-Hole Recombination Rate in Metal Halide Perovskites. *Energy Environ. Sci.* **2018**, *11*, 101–105.
- (41) Kirkwood, J. G. Statistical Mechanics of Fluid Mixtures. *J. Chem. Phys.* **1935**, *3*, 300–313.
- (42) Liang, Y.; Tsubota, T.; Mooij, L. P.; Van de Krol, R. Highly Improved Quantum Efficiencies for Thin Film BiVO_4 Photoanodes. *J. Phys. Chem. C* **2011**, *115*, 17594–17598.
- (43) Abdi, F. F.; van de Krol, R. Nature and Light Dependence of Bulk Recombination in Co-Pi-Catalyzed BiVO_4 Photoanodes. *J. Phys. Chem. C* **2012**, *116*, 9398–9404.
- (44) Abdi, F. F.; Firet, N.; van de Krol, R. Efficient BiVO_4 Thin Film Photoanodes Modified with Cobalt Phosphate Catalyst and W-doping. *ChemCatChem* **2013**, *5*, 490–496.
- (45) Cooper, J. K.; Gul, S.; Toma, F. M.; Chen, L.; Glans, P.-A.; Guo, J.; Ager, J. W.; Yano, J.; Sharp, I. D. Electronic Structure of Monoclinic BiVO_4 . *Chem. Mater.* **2014**, *26*, 5365–5373.
- (46) Ambrosio, F.; Wiktor, J.; Pasquarello, A. pH-dependent Surface Chemistry from First-Principles: Application to the $\text{BiVO}_4(010)$ -Water Interface. *ACS Appl. Mater. Interfaces* **2018**, *10*, 10011–10021.
- (47) Ambrosio, F.; Wiktor, J.; Pasquarello, A. pH-dependent Catalytic Reaction Pathway for Water Splitting at the BiVO_4 -water Interface From the Band Alignment. *ACS Energy Lett.* **2018**, *3*, 829–834.
- (48) Zachäus, C.; Abdi, F. F.; Peter, L. M.; Van De Krol, R. Photocurrent of BiVO_4 is Limited by Surface Recombination, not Surface Catalysis. *Chem. Sci.* **2017**, *8*, 3712–3719.
- (49) 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.
- (50) Liu, H.; Yuan, J.; Jiang, Z.; Shangguan, W.; Einaga, H.; Teraoka, Y. Novel Photocatalyst of V-Based Solid Solutions for Overall Water Splitting. *J. Mater. Chem.* **2011**, *21*, 16535–16543.