Small polarons and the Janus nature of TiO₂(110)

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Polarons are ubiquitous in many semiconductors and have been linked with conductivity and optical response of materials for photovoltaics and heterogeneous catalysis, yet it remains unclear how surface polarons influence adsorption. Here, by modeling the surface of rutile titania using density functional theory, we reveal the effect of small surface polarons on water adsorption, dissociation, and hydrogen bonding. On the one hand, the presence of such polarons significantly suppresses dissociation of water molecules that are bonded directly to polaronic sites. On the other hand, polarons facilitate water dissociation at certain nonpolaronic sites. Furthermore, polarons strengthen hydrogen bonds, which in turn affects water dissociation in hydrogen-bonded overlayer structures. This study reveals that polarons at the rutile surface have complex, multifaceted, Janus-like effects on water adsorption, dissociation, and hydrogen bonding, highlighting the importance of polarons on water structure and dynamics on such surfaces. We expect that many of the physical properties of surface polarons identified here will apply more generally to surfaces and interfaces that can host small polarons, beyond titania.

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The fundamental physics of defects at clean surfaces and aqueous interfaces is of great importance to everyday processes such as wetting and nucleation, as well as the more application-oriented topics of photovoltaics and heterogeneous catalysis [1–4]. Atomic defects on metal oxides, such as oxygen vacancies and interstitials, have received the most interest, and they are often considered to increase surface activity [5–15]. Polarons are another important class of defects that have recently been highlighted and linked to the activity of titania [16–19], ceria [12], and haematite [10,20]. Polarons are quasiparticles consisting of localized electrons bound to lattice distortions, and in a so-called small polaron this coupling is localized to within one or two lattice spacings. They are particularly important in metal oxides, where they can be generated through photoabsorption or via reducing defects such as oxygen vacancies and cation interstitials [6,8–12,20]. The physical properties of polarons can be very different from those of excess electrons, leading to strong modifications of the properties of materials [21–23]. Of the oxide surfaces where polarons are known to be important, the (110) surface of rutile TiO₂ has received the most attention, as a model system but also because of its broad importance to

photocatalysis and photovoltaics [1,24,25]. Recently, several studies on TiO₂ have shown that the surface segregation and dynamics of polarons can be observed in real space [16,17,26–30], and that surface polarons and adsorbates influence each other.

The above observations raise the question of how water is affected by small polarons on the rutile (110) surface. This is an important question because even on well-prepared samples, the structure and dissociation states at the aqueous interface of rutile (110) are still under debate; see, e.g., Refs. [24,31–34]. Water dissociation is often affected by specific atomic defects such as oxygen vacancies, as mentioned above, making it difficult to establish the intrinsic properties of stoichiometric TiO₂ [35–40]. For example, photoelectron spectroscopy and diffraction studies show evidence of a dissociation channel on rutile (110), suggesting that water dissociates without defects [41,42]. But measurements by Wang *et al.* and other microscopic surface experiments are in favor of water not dissociating on nondefective rutile (110) surfaces [24,43]. Considering the fact that polarons are major charge carriers in such systems [17,27–29], establishing the general role of polarons on water could bridge the gap between our knowledge of pristine surfaces and surfaces with various specific defects.

In this study, we employ density functional theory (DFT) to investigate the role of polarons at the water-rutile (110) interface. We find a significant site dependence for both intact and dissociated water adsorption, leading to a direct suppression of water dissociation on polaronic sites and an indirect enhancement of dissociation at nonpolaronic adsorption sites. We also examine how polarons influence the hydrogen bonds (HBs) between adsorbed water molecules, and we discuss how this indirectly affects water dissociation. Overall, we

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see that polarons have a surprisingly rich influence on the properties of wet titania. This behavior is likely to hold for other adsorption systems and interfaces, and indeed we show that methanol on $\text{TiO}_2(110)$ is also strongly influenced by polarons. The polaronic effects identified in this study could be relevant to the interfacial structure and the photocatalytic efficiency of other materials beyond titania. In this study, most calculations were carried out using the VASP package [44].

The primary means by which polarons were introduced into TiO_2 was by adding an excess electron, with a compensating background charge (see SI [45] for tests on the convergence of our results with respect to the size of the supercell and the vacuum). However, calculations in which polarons were introduced by an oxygen vacancy or a Ti interstitial were also performed. Projector augmented wave potentials were used with an energy cutoff of 500 eV, and for the Ti atom 12 electrons were treated as valence. The polaronic configurations were carefully optimized as discussed in the supporting information (SI) [45]. Indeed, the modeling of polarons with DFT methods has been heavily debated, mainly due to the challenging nature of localized $3d$ electrons (see, e.g., Refs. [7,46–50], and references therein). Here, to test the validity of our main conclusions, results are reported with several exchange correlation functionals, including the Heyd-Scuseria-Ernzerhof (HSE) hybrid exchange correlation functional [51,52], and the Perdew-Burke-Ernzerhof (PBE) functional [53] with the on-site Coulomb interaction correction approach of Dudarev *et al.* (PBE+U) [54]. *Ab initio* molecular-dynamics simulations were also performed, with the CP2K/QUICKSTEP package [55].

Full details of the computational setup are given in the SI [45], which includes additional Refs. [56–68]. Extensive tests were performed to ensure the validity of key conclusions that are based on calculated energy differences [45].

We begin by looking at the polaronic configurations and water adsorption structures on $\text{TiO}_2(110)$. Figures 1(a) and 1(b) shows the surface structure of $\text{TiO}_2(110)$, which can be characterized into rows of fivefold-coordinated titania (Ti_{5c}) and surface bridging oxygens (O_{br}). When an electron is added to the substrate, it localizes on a Ti_{5c} site as shown by the partial charge density [yellow lobes, Figs. 1(a) and 1(b)]. The localized electron distorts the lattice, and in the case of a small polaron this mostly involves elongation of the nearest Ti-O bonds by approximately 0.1 Å (Fig. S5). Ti_{5c} sites are polaron hosts and they are also adsorption sites for water, either in vacuum or at water- $\text{TiO}_2(110)$ interfaces (Fig. S7).

The adsorption structure of water on $\text{TiO}_2(110)$ has been discussed in many previous theoretical and experimental studies (see, e.g., Refs. [9,11,24], and references therein). Figure 1(c) shows the adsorption of an individual water molecule on a polaron, which is similar to the adsorption of water on a nonpolaronic Ti_{5c} site. The adsorption energy, E_{ad} , is defined as $E_{ad} = E_{\text{water/substrate}} - E_{\text{substrate}} - E_{\text{water}}$, where $E_{\text{water/substrate}}$ is the total energy of the adsorption system, $E_{\text{substrate}}$ is the total energy of the clear substrate, and E_{water} is the total energy of the gas-phase water molecule. With this definition and the PBE+U method we obtain an adsorption energy of -0.92 eV on the pristine surface. On the polaronic site, the adsorption energy of the water molecule is changed, compared to the pristine surface, to -0.94 eV. The presence of a localized

FIG. 1. Polaronic configurations and water monomer adsorption structures on rutile (110). Part (a) is a side view of the rutile (110) surface with a surface polaron. Ti_{5c} is the fivefold-coordinated surface titanium and O_{br} is the surface bridging oxygen. Part (b) is a top view of the polaronic rutile (110) surface, which can be characterized into rows of Ti_{5c} and O_{br} . The yellow isosurface shows the partial charge density of the polaron, and the green circle and arrows indicate that the polaron is a small polaron, where mostly the nearest Ti-O bonds are elongated by approximately 0.1 Å. The partial charge density is the charge density from the polaron state as shown by the gap state of Fig. S2b. Parts (c) and (d) show the side view of an adsorbed water molecule and a dissociated water molecule on the polaron, respectively.

polaron breaks the equivalence of the adsorption sites, and in the neighborhood of the polaron a range of water adsorption energies is found. This is shown by the heat map of water molecule adsorption energies on Ti_{5c} sites in Fig. 2(a). Interestingly, it can be seen from Fig. 2(a) that water adsorption on nonpolaronic sites can be significantly destabilized, with the largest suppression up to ~ 170 meV. Overall we see that water molecule adsorption at the polaronic site is favored over the nonpolaronic sites.

Dissociation of a water molecule leads to the adsorption configuration of Fig. 1(d), consisting of a bridging hydroxyl group (O_{br}H) and a terminal hydroxide group (O_{th}H). On the same polaronic substrate as discussed above, the O_{th}H can adsorb on the polaronic site [Fig. 1(d)] or on nonpolaronic sites. The site-dependent change in the O_{th}H adsorption energy is shown in Fig. 2(b). Compared with the adsorption of an intact water molecule, the adsorption of dissociated water is affected quite differently by the polaron. Specifically, (i) adsorption on the polaronic site is significantly suppressed by 0.22 eV; and (ii) adsorption on nonpolaronic sites is also suppressed but to a smaller extent, varying from 0 to 0.18 eV. This means that on a polaronic substrate, a dissociated water molecule shows an energetic preference for nonpolaronic sites over polaronic sites.

Considering the effects of polarons on molecular water and dissociated water together, we obtain a site-dependent dissociation energy ΔE [Fig. 2(c)], defined as $\Delta E = E_{\text{total}}(\text{dissociated}) - E_{\text{total}}(\text{molecular})$, where E_{total}

FIG. 2. The presence of localized polarons breaks the equivalence of the adsorption sites on the rutile (110) surface. (a) and (b) Heat maps of the change in adsorption energies (ΔE_{ad}) for molecular [Fig. 1(c)] and dissociated [Fig. 1(d)] water, respectively, upon introducing a polaron. Positive values indicate that polarons suppress adsorption. (c) Heat map showing the effect polarons have on the water dissociation energy (change of ΔE). Positive values indicate that dissociation is suppressed. In all three heat maps, the polarons are indicated with the black circles and periodic 2×4 unit cells are indicated with the green dashed box in panel (a). (d) Plots showing the effect polarons have on the adsorption energy of molecular water and dissociated water, and the dissociation energy on different sites as indicated in panel (a). All results in this figure are from the PBE+U methods; those denoted by the green dashed line are calculated using the HSE functional.

(dissociated) and $E_{total}(\text{molecular})$ are the total energies of the adsorption systems of a dissociated water molecule and an intact water molecule, respectively. On the polaronic sites, water dissociation is very strongly suppressed by ~ 240 meV. However, we also find that water dissociation at nonpolaronic sites can be affected either negatively or positively, by up to 30 meV [Fig. 2(d)]. Therefore, we see that polarons present two faces to the dissociation of water. On the one hand, a water molecule adsorbs preferentially on the polaronic site and dissociation is inhibited. On the other hand, there are nonpolaronic sites on a polaronic substrate where water dissociation is enhanced. This Janus-like behavior of $\text{TiO}_2(110)$ may affect the adsorption and dissociation of water at higher coverages when water molecules occupy both polaronic and nonpolaronic sites simultaneously, or in experiments where water molecules can be manipulated from one site to another. In addition, the polarons and the water are mobile and will likely have different temperature dependencies, thus it is important to understand water adsorption and dissociation directly at the polaron and at the nonpolaronic sites.

As noted above, the accurate modeling of polarons can be challenging (see, e.g., Refs. [7,46–50]), thus we performed a series of calculations with the HSE hybrid exchange correlation functional [open circles in Fig. 2(d)]. As with PBE+U, HSE shows a similar Janus-like behavior for water dissociation. Specifically, there is a significant suppression on the polaronic site and a possible enhancement of dissociation on several nonpolaronic sites. In addition, in the SI we show the results obtained with different U values and other exchange correlation functionals. Irrespective of the

exchange correlation functional used, Janus-like behavior is observed.

We note that the aim of this study is to investigate specifically the influence of polarons on water adsorption, and to decouple this from the influence that other defects, such as oxygen vacancies and Ti interstitials, can have. For instance, it is well known that water will dissociate at surface oxygen vacancies. Having specific defects such as oxygen vacancies and Ti interstitials may also make the nonpolaronic sites of the surface more complex to classify, because there one needs to take into account how far the nonpolaronic site is away from the defect. However, Fig. 3(a) shows the large suppression role of water dissociation on polaronic sites for polarons created by means of surface oxygen vacancies (Fig. S3) and Ti interstitials (Fig. S4). This shows that the suppression role is a physical effect of polarons and does not depend on how polarons are created.

Furthermore, we find that the suppression of water dissociation by polarons not only raises the dissociation energy, but also increases the dissociation barrier. Figure 3(b) plots the energy profile along the dissociation path of water on a pristine substrate and on a polaronic substrate calculated using the climbing image nudged elastic band method (cNEB) [69]. On the pristine substrate the energy barrier is 0.14 eV, while in the presence of polarons the barrier increases to 0.22 eV. There is also a significant reduction of the recombination barrier, from 0.18 eV to ~ 0.01 eV. Thus there is an almost negligible barrier to reverse dissociation on a polaronic surface site.

More often than not, water on surfaces adsorbs at higher coverages than isolated monomers, forming a rich variety of

FIG. 3. (a) The dissociation energy for a water monomer on TiO₂ using different exchange correlation functionals and models. The dissociation energy is defined as the total energy difference between the dissociated [Fig. 1(d)] and molecular [Fig. 1(c)] adsorption states. EE, OV, and TI indicate that the polarons are induced by an excess electron, an oxygen vacancy, and a Ti interstitial, respectively. (b) The energy profiles for water dissociation calculated with PBE+U on pristine and polaronic TiO₂ surfaces, computed with the nudged elastic band approach.

hydrogen-bonded structures [4]. To understand the influence of polarons in this regime, we considered a range of models from low to high water coverage, including monomers, dimers, a monolayer, and a liquid water film (detailed in the SI). Figure 4(a) summarizes the dissociation energy on the pristine and polaronic substrates for all models studied. First, we see that there is a suppressing effect of polarons for all adsorption structures considered, ranging from 20 to

FIG. 4. (a) The effect of polarons on water dissociation on surfaces with different water coverage. (c) The length of HBs and the valence charge on the pristine surface (blue) and the polaronic surface (orange). The HBs are shown with the green dashed lines in panel (b). Parts (b) and (d) are the charge rearrangement upon HB formation shown with the isosurfaces ($\pm 0.002 e \text{ Bohr}^{-3}$) of $\Delta \rho$ on the polaronic surface and the pristine surface, respectively. $\Delta \rho = \rho_{\text{surface+dimer}} + \rho_{\text{surface}} - \rho_{\text{surface+water}_1} - \rho_{\text{surface+water}_2}$ [70]. $\rho_{\text{surface+water}_1}$ and $\rho_{\text{surface+water}_2}$ are charge densities of the surface with the first and the second water molecule, respectively.

200 meV. Second, when the coverage is low and adsorbed water molecules are not hydrogen-bonded to each other, polaronic effects are rather similar to the monomer scenario discussed above, featuring a large suppression of water dissociation by approximately 200 meV. However, when HBs form between water molecules, the influence of polarons is more subtle and intimately connected with the nature of the HB.

We now discuss the effect of polarons on hydrogen bonding, which not only explains the complex behavior identified at high water coverage but also on its own is essential to, e.g., the structure, stability, and dynamics of water on surfaces. Using the flat dimer structure as an example [Figs. 4(b) and 4(d)], dissociation leads to the formation of an H₂O-OH group. In this adsorption complex, there are two HBs (one internal and one between the OH and the bridging hydroxyl). Both are affected by the polaron. Specifically, as shown in Fig. 4(c), they are shortened and hence strengthened by polaron doping. Analysis shows that this is because the valence charge on the terminal oxygen increases, making it a better HB acceptor. Figures 4(b) and 4(d) show the charge rearrangement upon the formation of the HB within the H₂O-OH group on the polaronic and the pristine surface, respectively [70]. The slight enhancement in the charge rearrangement also indicates the strengthening of the HB. For the molecular water dimer, HBs are enhanced by polarons as well, but to a much lesser extent. Therefore, the fact that polarons enhance HBs in H₂O-OH more than HBs in the water dimer effectively limits the suppression effects to water dissociation. Note that a more quantitative determination of the hydrogen bond strength and its change due to polarons would require careful consideration of the performance of DFT methods on hydrogen bonds [71].

The observation that polarons increase HB strengths also applies to other models studied here. For example, the HB between the water monomer and the surface bridging oxygen shrinks from 1.76 to 1.71 Å for molecular water and from 2.02 to 1.62 Å for the dissociated structure upon the addition of polarons. For more complicated systems, such as the vertical dimer (a dimer structure extracted from the liquid), the monolayer, and the liquid film models, the suppression effects on water dissociation and the enhancing effects on HBs play off against each other. The overall effects are sensitive to the specific models employed, but qualitatively for all models studied water dissociation is suppressed on the polaronic sites. In the discussions above, we have shown that nonpolaronic sites on polaronic surfaces can enhance water dissociation. In the SI we show that such effects remain in hydrogen-bonded systems.

Let us now connect our results to experiments. First, there is already support for one aspect of our observations in recent experiments. In a previous study, some of us observed the segregation of polarons toward the water-covered rutile (110) surface using photoemission spectroscopy [17]. The observations indicate an attractive water-polaron interaction, which is consistent with the enhanced water adsorption and enhanced HB strength shown in this study. Second, our results might help to rationalize some of the debates associated with water on TiO₂. Given the ability of polarons to both inhibit and enhance dissociation, and the fact that polarons are mobile and that this mobility will depend on temperature, it is now easier to see how different measurements could

yield different conclusions in terms of water dissociation [24,35,37,38,41–43]. In addition, the interfacial structure at the rutile (110) water interface is still highly debated (see, e.g., Refs. [33,34]). Understanding the polaronic effects on the adsorption of water/hydroxide and the strength of HBs may shed light on this issue that the stability of interfacial water might be affected by polarons induced in experiments. We are certainly not saying that polarons are the full story in terms of the water structure and dissociation debates, but our results suggest that they are likely to be more relevant than previously anticipated.

Beyond water on rutile, in the SI we show that polaronic effects can be extended to the dissociation of methanol on rutile, a system of importance to heterogeneous catalysis [72]. Indeed, there are many other polaronic substrates such as ceria and haematite that can host small polarons, and dissociation on the surfaces of these materials is key to processes in heterogeneous catalysis [73,74]. Our study suggests that the adsorption and dissociation of molecules should be discussed in the context of different sites on polaronic substrates. On other polaronic substrates, the binding of a water molecule to polaronic sites will likely lead to the suppression effect observed here, and nonpolaronic sites may behave in a more complex manner. Overall, differences are also expected going from the (110) surface of rutile TiO_2 to other polaronic surfaces and materials, and the interplay between polarons and adsorbates has yet to be established. Finite-temperature effects on both the thermodynamics and the dynamics may further affect the interactions of polaron on adsorbates.

To conclude, this study has revealed various key roles played by polarons in the rutile (110) surface on water adsorption, dissociation, and hydrogen bonding. First, such polarons significantly modulate the adsorption of water and hydroxide groups on the surface. Consequently, they suppress the dissociation of adsorbed water molecules on polaronic sites, while on nonpolaronic sites the effects are less significant, and even a slight enhancement is possible, showing a multifaceted Janus-like behavior. The suppressing effect extends to higher water coverage and aqueous interfaces. In addition, we find that water molecules and hydroxide groups become better HB acceptors when bonded to polarons. Overall, our study should encourage additional high-resolution experiments and advanced theoretical simulations to disentangle the key polaronic features affecting heterogeneous physical systems and processes.

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