Quasiparticle interfacial level alignment of highly hybridized frontier levels: H₂O on TiO₂(110)

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ABSTRACT: Knowledge of the frontier levels’ alignment prior to photo-irradiation is necessary to achieve a complete quantitative description of H₂O photocatalysis on TiO₂(110). Although H₂O on rutile TiO₂(110) has been thoroughly studied both experimentally and theoretically, a quantitative value for the energy of the highest H₂O occupied levels is still lacking. For experiment, this is due to the H₂O levels being obscured by hybridization with TiO₂(110) levels in the difference spectra obtained via ultraviolet photoemission spectroscopy (UPS). For theory, this is due to inherent difficulties in properly describing many-body effects at the H₂O–TiO₂(110) interface. Using the projected density of states (DOS) from state-of-the-art quasiparticle (QP) G₀W₀, we disentangle the adsorbate and surface contributions to the complex UPS spectra of H₂O on TiO₂(110). We perform this separation as a function of H₂O coverage and dissociation on stoichiometric and reduced surfaces. Due to hybridization with the TiO₂(110) surface, the H₂O 3a₁ and 1b₁ levels are broadened into several peaks between 5 and 1 eV below the TiO₂(110) valence band maximum (VBM). These peaks have both intermolecular and interfacial bonding and antibonding character. We find the highest occupied levels of H₂O adsorbed intact and dissociated on stoichiometric TiO₂(110) are 1.1 and 0.9 eV below the VBM. We also find a similar energy of 1.1 eV for the highest occupied levels of H₂O when adsorbed dissociatively on a bridging O vacancy of the reduced surface. In both cases, these energies are significantly higher (by 0.6 to 2.6 eV) than those estimated from UPS difference spectra, which are inconclusive in this energy region. Finally, we apply self-consistent QPGW (scQPGW1) to obtain the ionization potential of the H₂O–TiO₂(110) interface.

1. INTRODUCTION

The photooxidation activity of a surface is determined by the interfacial level alignment between the occupied adsorbate levels and those of the substrate. Water photooxidation on TiO₂ has attracted enormous attention for energy applications. This reaction also plays an important role in photocatalytic environmental remediation and surface self-cleaning/sterilizing. This is because the resulting hydroxyl radicals are the key intermediates in the oxidative degradation of organic species. To understand water photooxidation, it is necessary to understand the interfacial level alignment between the occupied levels of H₂O and the TiO₂ substrate.

Experimentally, the most common approach to access the adsorbate levels is to take the difference between the covered and clean surface spectra from photoemission spectroscopy. However, when the adsorbate and surface levels are strongly hybridized, it becomes difficult to disentangle the adsorbate and surface contributions to the UPS spectra using only the difference spectra. For example, shifting of the surface levels due to hybridization or band bending may completely obscure the adsorbate levels. Further, the adsorbate levels near the valence band maximum (VBM) are the most likely to be obscured. It is precisely these levels that are most important for photooxidation processes. Using a theoretical approach, one can directly disentangle the molecular levels by projecting the density of states (DOS) of the interface onto the atomic orbitals of the molecule. Altogether, this makes a robust theoretical approach necessary to accurately predict the alignment of the adsorbate and substrate levels, and separate the adsorbate and surface spectra.

A robust theoretical treatment requires quasiparticle (QP) G₀W₀ to capture the anisotropic screening of the electron–electron interaction at the interface. As previously demonstrated for CH₃OH on TiO₂(110), QP G₀W₀ is necessary to obtain even a qualitative description of the level alignment. For this interface, the occupied levels of the molecule are only weakly hybridized with the surface levels. This allowed an unambiguous comparison to the photoemission difference spectrum. However, for H₂O on rutile...
TiO$_2$(110), this is not the case.

The occupied molecular levels of H$_2$O on single crystal rutile TiO$_2$(110) have been probed via ultraviolet photoemission spectroscopy (UPS) and metastable impact electron spectroscopy (MIES). These experiments were performed under ultrahigh vacuum (UHV) conditions from low to room temperature, and for various surface preparations resulting in either reduced TiO$_{2-x}$(110) with surface oxygen defects or “nearly-perfect” TiO$_2$(110). Altogether, these experiments have addressed the long-standing controversy as to where and how H$_2$O adsors and dissociates on TiO$_2$(110).

At 150 K the photoemission difference spectrum between H$_2$O covered and clean TiO$_2$(110) surfaces consists of three peaks, which are attributed to intact H$_2$O adsorbed on Ti coordinately unsaturated sites (Ti$_{cat}$). Upon heating to 300 K, the difference spectrum’s three-peak structure evolves into a two-peak structure, which is attributed to dissociated H$_2$O adsorbed on bridging O vacancies (O$_{br}$), i.e., O$_{br}$H surface species. This assignment of the UPS spectra to intact (I) H$_2$O@Ti$_{cat}$ or dissociated (D) H$_2$O@O$_{br}$ is based on the peak energy separations being consistent with those reported for H$_2$O in gas phase or OH" in NaOH.

A comparison to the H$_2$O and OH" peaks is robust for the molecular levels that lie below and have little hybridization with the surface DOS. However, the adsorbate levels that lie within the surface valence band may significantly hybridize with the surface, with a single molecular level contributing to many interfacial levels. These interfacial levels are thus not easily associated with H$_2$O and OH" levels. This is exacerbated by the mixing of the molecular levels due to symmetry breaking at the interface. As a result, “between 5 and 8 eV” below the Fermi level, experimentally they are unable to produce reliable difference structures from the UPS spectra obtained for “nearly-perfect” TiO$_2$(110) exposed to H$_2$O at 160 K.

Using the QP $G_0W_0$ H$_2$O projected DOS (PDOS), we have disentangled the adsorbate and surface contributions to the UPS spectra within this difficult energy range. This has been done as a function of H$_2$O coverage and dissociation on stoichiometric and reduced surfaces. In so doing, we provide quantitative values for the energies of the highest H$_2$O occupied levels, prior to photo-irradiation, for a number of experimentally relevant H$_2$O-TiO$_2$(110) structures.

To directly compare to red-ox potentials, the important quantities for determining photoelectrocatalytic activity, one needs the alignment relative to the vacuum level, $E_{vac}$, with $E_{vac}$ = $E_{0_{vac}} + E_{PDOS}$. With this, one obtains the ionization potential directly from $E_{peak}$ + $E_{vac}$. To obtain a more accurate absolute level alignment, we employ our recently introduced self-consistent QP GW approximation scQPWGW. The presentation of the results is organized as follows. First, we focus on the H$_2$O levels that lie below and have little hybridization with the substrate DOS. This is done for intact H$_2$O@Ti$_{cat}$ in Section 3.1 and dissociated H$_2$O@O$_{br}$ in Section 3.2. Further, in Section 3.3, we show that these results are rather independent of the choice of xc-functional. In so doing we provide evidence for a robust semi-quantitative agreement with the UPS difference spectra for the adsorbate levels for which an unambiguous comparison with the experiment is possible. For a more complete understanding of the UPS experiments, in Section 3.4 we analyze the H$_2$O PDOS for a variety of other H$_2$O structures on the stoichiometric and reduced surfaces. These may form under different experimental conditions and surface preparations. In Section 3.5 we focus on the highest H$_2$O occupied levels, which are significantly hybridized with the substrate DOS. The success of the QP $G_0W_0$ PDOS strategy for the lower-energy part of the UPS difference spectra provides support for our results in this difficult spectral region, where a straightforward comparison with experiment is not possible. Finally, in Section 6 we employ scQPWGW to obtain an improved absolute level alignment relative to $E_{vac}$, and thus estimate the ionization potential of the H$_2$O-TiO$_2$(110) interface.

2. METHODOLOGY

Our QP $G_0W_0$ calculations have been performed using vasp within the projector augmented wave (PAW) scheme. The $G_0W_0$ calculations are based on Kohn-Sham wavefunctions and eigenenergies from density functional theory (DFT) obtained using a generalized gradient approximation (PBE) for the exchange correlation (xc)-functional. The dependence of the QP $G_0W_0$ DOS and PDOS on the DFT xc-functional has been tested for 1 ML intact H$_2$O@Ti$_{cat}$ of stoichiometric TiO$_2$(110) and 1/2ML dissociated H$_2$O@O$_{br}$ of defective TiO$_{2-x}$(110) with 1/2ML of O$_{br}$$. For these structures, QP $G_0W_0$ calculations based on the local density approximation (LDA) and the range-separated hybrid (HSE) xc-functionals have been carried out for comparison with the PBE based $G_0W_0$ calculations. In particular, we use the HSE06 variant of the HSE xc-functional.

In the QP $G_0W_0$ approach, the contribution to the Kohn-Sham (KS) eigenvalues from the exchange and correlation (xc)-potential $V_c$ is replaced by the self energy $\Sigma = \Sigma GW$, where $G$ is the Green’s function and $\Sigma$ is the screening based on the KS wavefunction. The dielectric function is obtained from linear response time-dependent (TD) density functional theory (DFT) within the random phase approximation (RPA), including local field effects. From $G_0W_0$ one obtains first-order corrections to the KS eigenvalues, but retains the KS wavefunctions. Since our aim is to compare the computed interfacial level alignment with measured UPS spectra, it is most consistent to align the QP $G_0W_0$ levels with the VBM.

We find $E_{vac}$, i.e., the effective potential far from the surface, from $G_0W_0$ is essentially the same as the $E_{vac}$ from DFT. In other words, the effective potential is unchanged by $G_0W_0$. To obtain a more accurate absolute QP level alignment relative to $E_{vac}$, we employ a self-consistent QP GW approach. In particular, by employing the scQPWGW approach, we obtain both a QP PDOS comparable to that from $G_0W_0$ and an improved alignment relative to $E_{vac}$. Here, 25%, 25%, and 50%, of the QP self energies are “mixed” with the DFT xc-potential over three self-consistent QP GW cycles, respectively. If, instead, 100% of the DFT xc-potential were replaced by QP self energy in a single self-consistent QP GW cycle, one would exactly obtain the QP $G_0W_0$ values, but retains the KS wavefunctions. Since our aim is to compare the computed interfacial level alignment with measured UPS spectra, it is most consistent to align the QP $G_0W_0$ levels with the VBM.

The geometries have been fully relaxed using LDA, PBE, or vdW-DF xc-functionals, with all forces $\leq 0.02$ eV/Å. HSE calculations are performed for the relaxed geometries obtained with PBE. We employ a plane-wave energy cuttoff of 445 eV, an electronic temperature $k_BT \approx 0.2$ eV with all energies extrapolated to $T \to 0$ K, and a PAW pseudopotential for Ti which includes the 3$s^2$ and 3$p^6$ semi-core levels. All calculations have been performed spin unpolarized.

For the clean stoichiometric TiO$_2$(110) surface we have used a four layer slab and an orthorhombic 1 × 1 unit cell of 6.497 × 2.958 × 40 Å$^3$, i.e.,

$$
\begin{pmatrix}
\sqrt{2}a & 0 & 0 \\
0 & c & 0 \\
0 & 0 & \sqrt{2}a + D
\end{pmatrix},
$$

where $D \approx 27$ Å is the vacuum thickness and $a$ and $c$ are the ex-
perimental lattice parameters for bulk rutile TiO$_2$ ($a = 4.5941$ Å, $c = 2.958$ Å). We have employed a Γ-centered $4 \times 8 \times 1$ k-point mesh, and 320 bands = 9/3 unoccupied bands per atom, i.e. including all levels up to 26 eV above the valence band maximum (VBM).

For the clean reduced TiO$_2$-$_{1/6}$(110) surface we have used a monoclinic $1 \times 2$ unit cell of $6.497 \times 5.916 \times 40$ Å$^3$, i.e.,

$$
\begin{pmatrix}
\sqrt{2} a & c & 0 \\
0 & 2c & 0 \\
0 & 0 & \sqrt{2}a + D
\end{pmatrix},
$$

(2)

to maximize the separation between the O$_{2uc}^{−}$... For the H$_2$O covered surfaces, we have employed a four layer slab with adsorbates on both sides and an orthorhombic $1 \times 2$ unit cell of $6.497 \times 5.916 \times 47$ Å$^3$, i.e.,

$$
\begin{pmatrix}
\sqrt{2}a & 0 & 0 \\
0 & 2c & 0 \\
0 & 0 & \sqrt{2}a + D
\end{pmatrix},
$$

(3)

where $D = 34$ Å. We employed a Γ-centered $4 \times 4 \times 1$ k-point mesh, with approximately 9/3 unoccupied bands per atom, i.e. including all levels up to 30 eV above the VBM, an energy cutoff of 80 eV for the number of G-vectors, and a sampling of 80 frequency points for the dielectric function. The $G_0W_0$ parameters are consistent with those previously used for describing rutile TiO$_2$ bulk, TiO$_2$(110) clean surface and interfaces.\cite{55,56} These parameters have been shown to provide accurate descriptions of bulk optical absorption spectra, and both clean surface and interfacial level alignment.\cite{55,56}

To model H$_2$O in the gas phase, we employed a unit cell with C$_2v$ symmetry and 16 Å of vacuum in each direction. At the $G_0W_0$ level, we used a smaller energy cutoff of 40 eV for the number of G-vectors, which has previously shown to provide an accurate description of the optical absorption spectra for isolated molecules.\cite{55,56}

To obtain DFT total energies and the relaxed structure of the clean reduced TiO$_2$-$_{1/6}$(110) surface we have used a monoclinic $1 \times 4$ unit cell of $6.497 \times 11.832 \times 28$ Å$^3$, i.e.,

$$
\begin{pmatrix}
\sqrt{2}a & 2c & 0 \\
0 & 4c & 0 \\
0 & 0 & \sqrt{2}a + D
\end{pmatrix},
$$

(4)

where $D = 15$ Å, and employed a Γ-centered $4 \times 2 \times 1$ k-point mesh.

In this study, we have performed PBE and subsequent single-point RPBE\cite{57,58} based DFT calculations for the H$_2$O adsorption energies $E_{ads}$ on the stoichiometric and reduced surfaces. The RPBE xc-functional was especially developed for the prediction of adsorption properties on metal surfaces.\cite{58}

The H$_2$O adsorption energy on the Ti$_{1uc}$ site of a stoichiometric TiO$_2$(110) surface is given by

$$
E_{ads} = \frac{E[nH_2O + TiO_2(110)] - E[TiO_2(110)]}{n} - E[H_2O],
$$

(5)

where $n$ is the number of adsorbed H$_2$O functional units in the supercell, and $E[nH_2O + TiO_2(110)]$, $E[TiO_2(110)]$, and $E[H_2O]$ are the total energies of the covered and clean stoichiometric surfaces and gas phase water molecule, respectively. Similarly, the H$_2$O adsorption energy on the O$_{2uc}$ site of a reduced TiO$_2$-$_{1/4}$(110) surface is given by

$$
E_{ads} \approx \frac{E[nH_2O + TiO_2-(110)] - E[TiO_2-(110)]}{n} - E[H_2O],
$$

(6)

where $E[nH_2O + TiO_2-(110)]$ and $E[TiO_2-(110)]$ are the total energies of the covered and clean reduced surfaces, respectively.

3. RESULTS AND DISCUSSION

3.1. Intact H$_2$O on the Stoichiometric Surface. In Figure 1 we disentangle adsorbate and substrate contributions to the spectrum of intact H$_2$O@Ti$_{1uc}$, and compare the H$_2$O PDOS to the theoretical and experimental difference DOS. Specifically, we model a monolayer (ML) of H$_2$O molecules with parallel ( 아니다) interfacial hydrogen bonds aligned along the [001] direction (Figure 1(a)). Note that 1ML of intact H$_2$O is the most stable coverage and structure on the stoichiometric rutile TiO$_2$(110) surface.\cite{19}

The theoretical difference DOS is the difference between the total DOS of the H$_2$O covered (H$_2$O@Ti$_{1uc}$) and clean stoichiometric (TiO$_2$(110)) surfaces, as shown schematically in Figure 1(a). Turquoise areas in the H$_2$O@Ti$_{1uc}$ and difference DOS indicate regions of greater density for the H$_2$O covered versus clean stoichiometric surface. The gray area indicates the DOS energy range for the clean stoichiometric TiO$_2$(110) surface. Figure 1(c) and (d) show two sets of UPS difference spectra obtained either by raising the temperature (from 150 K to 190 K) for a consistent exposure to H$_2$O (0.2 L) for an annealed TiO$_2$(110) surface, or by increasing the H$_2$O dose (from 0.1 L to 1 L) at low temperature (160 K) for a nearly perfect surface.\cite{19} The experimental spectra have been referenced to the VBM, which is positioned...
These peaks split due to mixing with the 3a character in the TiO$_2$ −3.2 eV below the experimental Fermi level. This hybridization with the surface has been severely underestimated by previous cluster-based MP2 calculations. Within the TiO$_2$(110) DOS region, the peaks in the H$_2$O PDOS have corresponding peaks in the difference DOS, although the relative peak intensities differ substantially between the two methods. More importantly, the difference DOS has dips centered at −4.1, −2.4, and −1.1 eV, where there are adsorbate levels in the PDOS, and a peak at −0.4 eV, where there are no adsorbate levels in the PDOS. The dips at −4.1 and −1.1 eV correspond to the O 2p$_\pi$ and O 2p$_\sigma$ peaks in the TiO$_2$(110) DOS, respectively, as marked in Figure 1(a). These peaks split due to mixing with the 3a$_1$ and 1b$_2$ H$_2$O orbitals. This splitting is the origin of the observed dips in the difference DOS, which are also seen experimentally in Figure 1(c) and d.

The peak at −9.4 eV in the H$_2$O PDOS, which has 1b$_2$ molecular character, agrees semi-quantitatively with the most strongly bound experimental peaks at −9.8 eV (Figure 1(c)) or −10.0 eV (Figure 1(b)). The peak at −6.3 eV in the H$_2$O PDOS, which has intermolecular 3a$_1$ bonding character, agrees semi-quantitatively with the experimental peaks at −6.4 eV (Figure 1(b)) or −7.1 eV (Figure 1(b)). Note that the theoretical average deviation is within that amongst the experiments. This may reflect differences in sample preparation, which result in a variety of different H$_2$O configurations, i.e., H$_2$O coverages, O$_{br}$ concentrations, and mixtures of intact and dissociated H$_2$O. As we will show in Section 3.4 by considering a variety of H$_2$O structures a more complete description of the experiment is obtained. Altogether, this agreement for the −9.4 and −6.3 eV PDOS peaks lends confidence to our results for regions where the experimental results are unclear.

The assignment of the peaks located within the TiO$_2$(110) DOS is much more complicated. The assumption that the highest peak in the experimental spectra originates solely from the H$_2$O 1b$_1$ level is an oversimplification. In fact, both the 3a$_1$ and 1b$_1$ molecular levels contribute within this region (Figure 1(b)). While the levels with intermolecular 3a$_1$ bonding character give rise to a distinct peak below the TiO$_2$(110) DOS region, those with intermolecular 3a$_1$ antibonding character are pushed to higher energies and mixed with the 1b$_1$ molecular levels (Figure 1(b)). The latter is due to symmetry breaking at the interface. Consequently, the H$_2$O PDOS is broadened into several peaks between −5 and −1 eV. These levels have interfacial (3a$_1$/1b$_1$− O 2p$_\sigma$/2p$_\pi$) and antibonding character (not visible at the isosurface value used).

### 3.2. Dissociated H$_2$O on Reduced Surfaces.

To see how dissociation of H$_2$O@O$_{br}$ affects the spectrum, we now consider 1/2 ML of H$_2$O dissociated on a reduced TiO$_2$−1/2(110) surface (Figure 2). Here, we have used TiO$_2$−1/2(110) to denote a surface consisting of 1/2 ML of O$_{br}$ defects. This structure corresponds to the staggered O$_{br}$H species, shown in Figure 2(b).

The theoretical difference DOS is the difference between the total DOS of the H$_2$O covered (H$_2$O@O$_{br}$) and the clean reduced (TiO$_2$−1/2(110)) surfaces, shown schematically in Figure 2(a). Turquoise areas in the H$_2$O@O$_{br}$ DOS and difference DOS indicate regions of greater density for the H$_2$O covered versus clean reduced surface. The gray area indicates the DOS energy range for the clean reduced TiO$_2$−1/2(110) surface. The O$_{2w}$ defects give rise to occupied levels with Ti 3d character that are just below the conduction band minimum and outside the energy range shown. Note that the H$_2$O PDOS includes half the O atoms and all the H atoms that make up the O$_{br}$H species. In this way the PDOS is provided in terms of H$_2$O formula units.

The peak in the difference DOS and PDOS at −7.0 eV has O$_{br}$H $\sigma$ character, as shown in Figure 2(b). Note that the peak intensity in the PDOS is about half that in the difference DOS, as the PDOS includes half the O$_{br}$ atoms. This peak’s position agrees semi-quantitatively with the experimental peaks at −7.1 (Figure 2(e)), −7.6 (Figure 2(f)), or −7.2 eV (Figure 2(g)). The PDOS has a broader feature between −4 and −1 eV, due to hybridization with the surface. This feature is associated with contributions coming from the bonding and antibonding combinations of two distinct $\sigma$ orbitals of the O$_{br}$H species (Figure 2(b)): one perpendicular to the O$_{br}$H $\sigma$ bonds (the so-called OH $\pi$ level of NaOH), the other in the plane of the O$_{br}$H $\sigma$ bonds. The lowest of these peaks at −3.9 eV corresponds to the bonding combination of the O$_{br}$H $\pi$ levels. This peak’s position agrees semi-quantitatively with the consistently observed experimental peaks at −4.8, −4.4, and −4.5 eV in Figures 2(e), 2(f), and 2(g), respectively. However, the antibonding O$_{br}$H $\pi$ levels are shifted to much higher energies (−1.2 eV), as shown in Figure 2(b).

Much of the theoretical difference DOS’s structure is attributable to the defect healing of O$_{2w}$, as seen from the difference DOS between TiO$_2$(110) and TiO$_2$−1/2(110) in Figure 3. This suggests that the observed features in the experimental difference spectra over-
long-ranged van der Waals interactions (vdW-DF) with (b,c) (d) (e)(a) 25 ε maximum, surface levels unrelated to the presence of H atoms. is usually attributed to O introduced by dissociated H using the (b) local density approximation (LDA) (d,e) generalized gradient approximation (PBE) (f,g) long-ranged van der Waals interactions (vdW-DF) for the xc-functional. The calculated H2O PDOS are compared with the UPS spectrum at 150 K after 0.2 L exposure (black). Energies are relative to the valence band maximum, εVBM.

Table 1. Height of H2O Above TiO2(110) for 1ML Intact H2O@Ti2x Measured with SXPS and Calculated with LDA, PBE, or vdW-DF XC-Functionals.

| Method   | d[H2O−Ti2x] (Å) |
|----------|-----------------|
| SXPS     | 2.210           |
| LDA      | 2.180           |
| PBE      | 2.367           |
| vdW-DF   | 2.434           |

lapping with the reduced surface’s DOS are simply Obr levels reintroduced by dissociated H2O@Ovac. In particular, the peak which is usually attributed to Obr H π levels is actually composed of Obr surface levels unrelated to the presence of H atoms.

3.3. XC-Functional and Methodology Dependence of H2O Spectra for Stoichiometric and Reduced Surfaces. To assess the robustness of the calculated QP H2O PDOS, we consider its dependence on the xc-functional and methodology. Specifically, we compare the H2O PDOS from DFT, scQPW1, and G0W0 for 1ML intact H2O@Ti2x with parallel (Figures 4, 5, and 6) (b,d,e). For G0W0 using the (b,d) generalized gradient approximation (PBE) (d,e) range-separated hybrid (HSE06) for the xc-functional. The calculated H2O PDOS are compared with the UPS spectrum at 150 K after 0.2 L exposure (black). Energies are relative to the valence band maximum, εVBM.

generated gradient approximation (PBE) long-ranged van der Waals interactions (vdW-DF) or a range-separated hybrid (HSE06) are employed for the xc-functional. This is consistent with the previously reported similarities between PBE and HSE based G0W0 PDOS for CH3OH on TiO2(110). This is despite the greater differences observed amongst the DFT H2O PDOS, which all differ qualitatively from the experiments. Furthermore, the G0W0 H2O PDOS is robust to the resulting changes in the H2O height above the surface, i.e., the distance between H2O and Ti2x d[H2O−Ti2x], shown in Table 1. Furthermore, Figure 5 (d,e) shows that scQPW1 provides a similar H2O PDOS level alignment to G0W0. This is consistent with what was previously reported for the CH3OH−TiO2(110) interface.

We clearly see that the differences between the DFT and G0W0 PDOS, i.e., the QP energy shifts, are far from simply being rigid. For instance, we find for PBE that the QP energy shifts for the levels that contribute to the highest-energy PDOS peak εpeak are almost negligible (cf. Figures 4(d,e) and 5(b,e)). As a result, the QP G0W0 εpeak is only ~0.1 eV lower compared to DFT. On the other hand, we find significant QP shifts to stronger binding for the levels that contribute to the most strongly bound PDOS peak with
As previously shown for the CH$_3$OH–TiO$_2$(110) interface, these differences in the shifts of the peaks are directly related to differences in the spatial distribution of the wave functions for the levels contributing to the peaks.\cite{6,35} This is because the QG$_W$$_0$ corrections to the DFT eigenenergies for interfaces are directly correlated with the spatial distribution of the wave function.\cite{52,53} The negligible shift of the DFT highest-energy PDOS peak (Figures 4(b,d,f) and 5(b,e)) is due to its strong hybridization with the surface, i.e., weight on TiO$_2$(110), for the levels contributing to this peak.\cite{52,53} On the other hand, the levels that contribute to the most strongly bound PDOS peak have little weight on TiO$_2$(110), and have $\sigma$ character. Both their localized H$_2$O character as well as their $\sigma$ nature explain why these levels have large QP energy shifts to stronger binding.\cite{23,24}

Oxygen defective and hydroxylated ($h-$)TiO$_2$ surfaces have occupied 3d levels which are associated with reduced Ti$^{3+}$ atoms.\cite{64} One such example is the 1/2ML dissociated H$_2$O@O$^{vac}_{br}$ on reduced TiO$_{2−1/2}(110)$ with 1/2ML of O$^{vac}_{br}$ shown in Figure 6(a). The spatial distribution of the 3d density for O defective surfaces has been characterized by low temperature scanning tunneling microscopy (STM).\cite{22,23} STM measurements find at 77 K the 3d density is homogeneously distributed along the [001] direction,\cite{34} while at $\sim$ 5 K the 3d density exhibits an asymmetric localized character.\cite{67}

A localized description of the Ti$^{3+}$ occupied 3d levels is not obtained from DFT with standard xc-functionals. For example, the occupied 3d levels obtained with PBE are highly delocalized, as clearly shown in Figure 6(b). This is due to self-interaction errors which are inherent in such xc-functionals. If one performs spin-polarized DFT calculations with a hybrid xc-functional on such systems, one obtains localized Ti$^{3+}$ 3d levels between 0.7 and 1.6 eV below the CBM, along with a structural deformation of the TiO$_2$(110) surface.\cite{63,65} However, spin-paired calculations with HSE06 on the PBE relaxed geometry only yield an occupied shoulder at the CBM (Figure 6(e)). At the QP QG$_W$$_0$ level based on PBE, this shoulder evolves into a distinct peak about 0.6 eV below the Fermi level, $E_F$. This effect is even more pronounced when the QG$_W$$_0$ calculation is based on HSE06 (cf. Figure 6(d,e)), which yields peaks at 0.6 and 0.9 eV below $E_F$. As compared to QG$_W$$_0$ PBE, QG$_W$$_0$ HSE06 shifts the unoccupied 3d levels further up in energy revealing the double peak structure. These energies are in very good agreement with the peak at 0.8 eV below $E_F$ in the UPS spectra of H$_2$O@O$^{vac}_{br}$ of Figure 2(d). This peak is not shown in Figure 2(d) as it is slightly above 2 eV with respect to VBM \cite{13} However, note that QG$_W$$_0$ overestimates by about 1 eV the VBM position relative to $E_F$ as compared with UPS experiments.\cite{13}

This result is completely independent of the wavefunction's spatial distribution, i.e., localization, as the QG$_W$$_0$ calculations are based on the KS wavefunctions. This is different from previous findings, which showed DFT with either PBE or hybrid xc-functionals is only giving distinct peaks for the occupied 3d levels provided the relaxed spin-polarized distorted structure is used in the calculations.\cite{63,65}

While for QG$_W$$_0$ based on PBE and HSE06 one sees noticeable differences in the description of the 3d occupied levels, the QP H$_2$O PDOS and its alignment relative to the VBM are unchanged. Although localization of the Ti$^{3+}$ occupied levels and associated structural deformations are absent from our approach, such features should not significantly alter the QP H$_2$O PDOS. This is because the Ti$^{3+}$ levels are too far above the VBM ($\sim$ 2 eV)\cite{61} to hybridize with the H$_2$O. Moreover, as we will show in Section 3.5, the QP H$_2$O PDOS is rather robust to local deformations of the surface structure, e.g., due to changes in coverage.

3.4. Coverage and Dissociation Dependence of H$_2$O Spectra for Stoichiometric and Reduced Surfaces. As different experimental conditions and surface preparations have been employed, there are expected to be different H$_2$O structures on the surface. To evaluate how strongly the DOS depends on the adsorption geometry, we now consider a variety of coverages of intact and dissociated H$_2$O on rutile stoichiometric TiO$_2$(110) (Figure 7) and reduced TiO$_{2−1/2}$ (110) (Figure 8) and TiO$_{2−4/2}$ (110) (Figure 9) with 1/2ML and 1/2ML of O$^{vac}_{br}$ defects, respectively. The relative importance of these geometries is illustrated in Figure 10(a) and 10(b) by the average absorption energy $E_{abs}$ per H$_2$O molecule on the stoichiometric or reduced surfaces\cite{25} with either PBE\cite{13} or RPBE\cite{57} xc-functionals. In so doing, the contribution of different structures to the measured spectra can be disentangled. Note that an intact 1/2ML of H$_2$O@O$^{vac}_{br}$ (Figure 8(b)) is probably only a transient locally stable state of the reduced H$_2$O–TiO$_{2−1/2}$(110) interface\cite{29} which may easily evolve into the $\sim$ 0.7 eV more stable dissociated 1/2ML H$_2$O@O$^{vac}_{br}$ (Figure 8(e)). For this reason, we only consider dissociated H$_2$O@O$^{vac}_{br}$ structures in Figure 10.

By comparing to lower coverage H$_2$O structures (1/2ML\cite{33,34} to 1ML\cite{31,39,98} in Figure 7 and 1/2ML\cite{31,39,98} to 2/2ML\cite{31,39,98} in Figure 8), we can disentangle the effect of interaction between the
H$_2$O molecules on the spectra. Further, these structures allow us to probe the isolated molecule limit.

As shown in Figure 10 at lower coverages the overall width of the spectra is reduced with fewer distinct peaks. When the coverage is increased to include intermolecular interactions between adjacent species, the molecular levels hybridize into bonding and antibonding intermolecular levels. This produces additional peaks above and below those present at low coverage. As a result, the peak with intermolecular bonding $3a_1$ character at $-6.3$ eV for 1ML of H$_2$O@Ti$_{cut}$ is absent for a ½ML coverage. This reinforces the assignment of the experimental spectra shown in Figure 1 to an intact 1ML H$_2$O@Ti$_{cut}$ geometry with interacting molecules.

To see how the spectra for dissociation of H$_2$O@Ti$_{cut}$ compare to H$_2$O@O$_{br}$, we have considered the half-dissociated (½D) and fully dissociated (D) H$_2$O structures shown in Figure 7. As shown in Figure 10(c), the peak at $-7.0$ eV with O$_{br}$H σ character for H$_2$O@O$_{br}$ splits into two peaks for dissociated H$_2$O@Ti$_{cut}$. The lower energy peak has both O$_{cut}$H and O$_{br}$H σ character, while the higher energy peak is mostly O$_{br}$H in character. Furthermore, we find a similar couple of peaks for ½ML mixtures of dissociated H$_2$O@O$_{br}$ and H$_2$O@O$_{cut}$ shown in Figure 10. This means one may recognize dissociated H$_2$O@Ti$_{cut}$ by both the presence of two peaks at about $-7.0$ and $-6.3$ eV, and the absence of the low-energy peak with 1b$_2$ character for intact H$_2$O@Ti$_{cut}$.

The absence of a peak at about $-6.3$ eV in the experimental spectra shown in Figure 2(e) reinforces its attribution to dissociated H$_2$O@O$_{cut}$ rather than dissociated H$_2$O@Ti$_{cut}$. This is further supported by the calculated H$_2$O absorption energies (Figure 10(a) and 10(b)). These are generally weaker for dissociated H$_2$O@Ti$_{cut}$, and stronger for H$_2$O@O$_{cut}$, as in previous calculations.

To check whether changes in the absorption geometry of H$_2$O affect the spectra for the same coverage, we compare 1ML of H$_2$O (1/½D, D) adsorbed with either parallel (±z) or antiparallel (±z) interfacial hydrogen bonds (black dashed lines in Figure 7). Overall, the two sets of spectra are consistent, and demonstrate the general robustness of the DOS to minor changes in the water absorption geometry. However, as the H$_2$O molecules are no longer equivalent when the interfacial hydrogen bonds are antiparallel, there is a greater splitting between bonding and antibonding contributions for the peaks with 1b$_2$ and 3a$_1$ molecular character. In particular, for intact H$_2$O, the lowest energy peak with molecular 1b$_2$ character splits with a separate peak at $-9.6$ eV, which is closer to the peaks at $-9.8$ (Figure 1(c) and $-10.0$ eV (Figure 1(d)) observed experimentally.

To see how increasing the H$_2$O coverage impacts the spectra, we compare monolayer (½ML, 1ML) to multilayer (½ML) H$_2$O (1/½D, D) (Figure 7) and consider the effect of additional H$_2$O@Ti$_{cut}$ to ½ML (Figure 8) and 1ML (Figure 9) H$_2$O@O$_{br}$. In this way we can see how robust the observed features in the individual spectra for isolated species are to screening by H$_2$O layers and probe the liquid water limit.

When a second layer of H$_2$O is added to the low coverage intact ½ML H$_2$O@Ti$_{cut}$ structure, the levels with H$_2$O 1b$_2$ character are unchanged, while the levels with 3a$_1$ and 1b$_1$ second layer character...
are more localized and weakly hybridized with the surface. These levels are seen as the two most intense peaks at ~−4.3 and −2.2 eV (Figure 10(e)). The former coincides with the peak at ~−4.2 eV observed experimentally at low temperatures (Figure 10(e)), suggesting multilayer H₂O structures may be present under these experimental conditions. The intermolecular H bonding between the layers delocalizes the molecular levels of the first layer. This is seen from the peak at ~−6.1 eV with antibonding 3a1 character on the first layer. We saw the same behavior when increasing the first layer’s coverage from ½ML to 1 ML. This is further confirmation that the peak observed experimentally at ~−6.4 eV has intermolecular character.

When a second ½ layer of H₂O is added to the 1ML H₂O@TiO₂ structures (½D, ⅔D) structures, a denser network of intermolecular and interfacial hydrogen bonds is formed, as shown in Figure 7. This causes a stronger hybridization between the OH and H₂O σ levels. For the ⅔D structure, this results in the four distinct σ peaks shown in Figure 7(e). On the one hand, the peaks at ~−9.1 and −6.2 eV have predominantly intact H₂O and Ocus⁻H character, as was the case for 1ML of ½D H₂O@TiO₂. On the other hand, the peaks at ~−7.9 and −7.4 eV are most related to the second layer. In effect, the H₂O σ level of the second-layer H₂O, which is fully saturated with four hydrogen bonds, is upshifted by more than an eV.

This is not the case for the ⅔D structure (Figure 7), where the peak at ~−9.1 eV instead has mostly intact second-layer H₂O H₂ character. As was the case for intact ½ML H₂O@TiO₂, the addition of a second ½ layer of H₂O induces a stronger hybridization of the Oσ levels, and introduces an additional intense peak at ~−4.4 eV (Figure 10(e)). This again suggests the experimentally observed peak at ~−4.2 eV (Figure 10(e)) may be due to multilayer H₂O.

Overall, we find the addition of second-layer H₂O affects the resulting spectrum qualitatively. We find both additional features and a redistribution of those due to the first H₂O layer. When we instead add H₂O@TiO₂ to the ⅔ML and ½ML H₂O@O¹° vac structures (Figures 9 and 8), we find the resulting spectrum is the sum of the separate spectra to within 0.2 eV (Figure 10). For example, the ½ML ⅔D spectrum (Figure 10(b)) for 1ML of intact H₂O added to ½ML H₂O@O¹° vac (Figure 8) is basically the sum of the 1ML intact H₂O@TiO₂ (Figure 10(a)) and ½ML H₂O@O¹° vac (Figure 2(a)) PDOS spectra downshifted by 0.2 eV. This explains the ease with which the experimental single-layer H₂O spectra may be analyzed for levels outside the surface DOS region.

### 3.5. Alignment of the Highest H₂O Occupied Levels

We have shown that the experimental peak at ~−4.2 eV is not, in fact, the highest energy peak of H₂O@TiO₂. We instead find the highest-energy PDOS peak (e_peak) for 1ML intact H₂O@TiO₂ at ~1.1 eV relative to the VBM (Figure 10(e)). This is 0.6 eV closer to the VBM than the ~−1.7 eV estimate deduced from the onsets of the UPS difference spectra in Ref. 18. Moreover, as 1ML H₂O@TiO₂ dissociates, e_peak moves up to ~1.0 eV (½D) and ~0.9 eV (D) (Figure 10(e)). This is again significantly higher than the ~−1.8 eV estimate based on UPS difference spectra for the TiO₂(100) surface from Ref. 7 where the charge transfer of ~0.4e⁻ that accompanies deprotonation (arrows in Figure 7). We find for the 1ML intact structure on TiO₂(110) e_peak is 0.2 eV closer to the VBM for H₂O than for CH₃OH. As was the case for CH₃OH on TiO₂(110), this raising of e_peak can be related to the charge transfer of ~0.4e⁻ that accompanies deprotonation (arrows in Figure 7). We find for the 1ML intact structure on TiO₂(110) e_peak is only ~0.1 eV lower compared to DFT estimates (Figure 4). After adding second-layer H₂O, e_peak is unchanged with weight mostly remaining on the first layer. We find for ½ML dissociated H₂O@O¹° vac e_peak ≈ −1.1 eV rel-

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**Figure 10.** Structure and coverage dependence of (a,b) adsorption energy E_ads and (c,d) G₀W₀ PDOS for H₂O adsorbed intact (I) or dissociated (D) on (a,c) coordinately unsaturated Ti sites (Ti_uns) of stoichiometric TiO₂(110) (Figure 7) and (b,d) bridging O vacancies (O¹° vac) of reduced TiO₂-x(110), with x = f (thin lines, Figure 9) or f/2 (thick lines, Figure 8). (a,b) E_ads calculated with PBE (○) and RPBE (●) xc-functionals for (white) low (½ and ⅔ML), (turquoise) medium (½ and 1ML), and (blue) high (⅔ and 1⅔ML) coverage. UPS difference spectra at (c) 150 K and (d) 300 K after 0.2 L exposure are from Ref. 25. (c,d) Energies are relative to the VBM (EᵥBM). Gray regions denote the clean surface DOS. Red dashed lines denote the highest PDOS peaks (e_peak) for 1ML H₂O@TiO₂ and ½ML H₂O@O¹° vac.
ative to the VBM (Figure 10), the same as for intact H$_2$O@Ti$_{\text{vac}}$.

This is much higher than the previous estimate of $\sim 3.7$ eV$^2$ for O$_{br}$H based on the UPS difference spectra in Ref. $^{25}$ Our corrected $\varepsilon_{\text{peak}}$ value agrees with the recently demonstrated photocatalytic importance of O$_{br}$H sites as the main oxidizing species on TiO$_2$(110).

Based on $\varepsilon_{\text{peak}}$ for 1ML intact H$_2$O@Ti$_{\text{vac}}$, vertical excitations from the highest H$_2$O occupied levels to the TiO$_2$(110) conduction band require photon energies that exceed the electronic band gap for bulk rutile TiO$_2$ (3.3 $\pm$ 0.5 eV$^{27}$) by $\geq 1$ eV. However, the hole generated by such super-band gap excitations should be mostly located on TiO$_2$(110) O 2$p_x$ rather than H$_2$O O 2$p_x$ levels. This is because the H$_2$O highest levels are hybridized with TiO$_2$(110) and are predominantly TiO$_2$(110) in character.

The fact that the highest H$_2$O levels are $\sim 1$ eV below the VBM does not necessarily mean that they cannot be photooxidized by holes photogenerated within the TiO$_2$(110) valence band. A recent DFT study with HSE06 found trapped holes at surface O sites, i.e., three-fold coordinated O$_{\text{fold}}$, are shared with nearby HO–Ti$_{\text{vac}}$ groups.

Moreover, it has been suggested that H$_2$O can only be photooxidized, i.e., trap a hole, upon deprotonation. In other words, hole transfer to the HO–Ti$_{\text{vac}}$ site should be mediated by the deprotonation of intact H$_2$O@Ti$_{\text{vac}}$ to the nearest O$_{br}$ site. Altogether, this suggests that H$_2$O@Ti$_{\text{vac}}$ photooxidation should be initiated by band-to-band and super-band photo-excitations, which result in the generation of holes within the TiO$_2$(110) valence band. These TiO$_2$(110) free holes may then be trapped at O$_{\text{fold}}$ sites, and partially transferred to nearby HO–Ti$_{\text{vac}}$ upon H$_2$O deprotonation.

3.6. Vacuum Level Alignment. So far, we have considered the level alignment of the interfacial levels relative to the VBM of the substrate. This allows a direct comparison of the occupied PDOS with the measured UPS spectra. However, to assess the photoelectrocatalytic activity of the interface, one needs the absolute level alignment relative to the vacuum level $E_{\text{vac}}$.

In Figure 11, we show the level alignment for gas phase H$_2$O and 1ML intact H$_2$O@Ti$_{\text{vac}}$ relative to $E_{\text{vac}}$ from DFT, scQPWG1, and G$_0$W$_0$ based on PBE and HSE xc-functionals. These are compared to the measured CBM for the liquid H$_2$O–TiO$_2$(110) interface, and the measured and coupled-cluster (CCSD(T)) gas phase H$_2$O ionization potential.

Our calculated IP values for H$_2$O in gas phase are consistent with those reported previously in the literature. Although the relative energies of the 1$b_1$, 3$a_1$, and 1$b_2$ H$_2$O levels are consistent over all five levels of theory, the levels are rigidly downshifted. We observe a clear ordering in increasing IP of PBE DFT (7.2 eV) $<$ HSE DFT $<$ PBE scQPWG1 $<$ PBE G$_0$W$_0$ $\leq$ HSE G$_0$W$_0$ $\leq$ PBE scQPWG1 (12.8 eV) $<$ Hartree Fock (HF) 13.9 eV$^{38}$.

To understand the origin of this ordering, we have probed the dependence of the IP on the parameter $\alpha$ in Figure 12. On the one hand, for DFT, we find a strong linear dependence of IP on $\alpha$, i.e., $IP \approx IP_{\text{PBE}} + (IP_{\alpha=1} - IP_{\text{PBE}})\alpha \approx 7.2 + 5.9\alpha$, with $\alpha \approx 0.9$ providing a quantitative agreement with experiment and CC(T) calculations. Overall, this linear dependence is not surprising, as $\alpha$ may be interpreted as the amount of electron-electron screening, i.e., the inverse dielectric constant $\varepsilon^{-1}$. In other words, the fraction of exact exchange $\alpha$ included, determines the amount of screening, $\varepsilon^{-1}$, incorporated within the xc-functional. The quantitative agreement of the IP for $\alpha \sim 0.9$ is because small molecules, e.g., H$_2$O$_2$, are weakly screened in the gas phase ($\varepsilon_{\text{vac}} \sim 1$).

On the other hand, for $G_0$W$_0$, the calculated IP has a much weaker dependence on $\alpha$, i.e., the starting xc-functional, with $IP \approx IP_{\alpha=1} - \Delta IP(10^{\alpha-1} - 1) \approx 13.4 - 1.2 \times 10^{-\alpha}$. Further, the $G_0$W$_0$ and

![Figure 11](image1.png)

**Figure 11.** Absolute level alignment for 1ML intact H$_2$O adsorbed with antiparallel (a) interfacial hydrogen bonds on coordinately unsaturated Ti sites (H$_2$O@Ti$_{\text{vac}}$). Total (magenta) and H$_2$O projected (blue) DOS computed with DFT, scQPWG1, and G$_0$W$_0$ using the generalized gradient approximation (PBE) and hybrid (HSE) xc-functionals. Energies are relative to the vacuum level $E_{\text{vac}}$. The measured $\varepsilon_{\text{CBM}}$ from Ref. 40 (thick gray line), measured and coupled-cluster (CCSD(T)) H$_2$O gas phase ionization potentials IP from Ref. 80 (thin gray line), and for each level of theory the calculated gas phase 1$b_1$, 3$a_1$, and 1$b_2$ H$_2$O levels (marked in cyan) are provided.

![Figure 12](image2.png)

**Figure 12.** Ionization potential IP versus exact exchange fraction $\alpha$ included in the HSE xc-functional and equivalent dielectric constant $\varepsilon_{\text{vac}} = \alpha^{-1}$ from DFT (filled symbols), G$_0$W$_0$ (open symbols), scQPWG1 (green filled symbols), and scQPWG (brown filled symbols) for H$_2$O in gas phase (circles), a clean (diamonds) and a 1ML of intact H$_2$O@Ti$_{\text{vac}}$ (squares) on the stoichiometric TiO$_2$(110) surface, and a 1/2ML of dissociated H$_2$O@O$_{br}$ (triangles) on the defective TiO$_2$-O$_{br}$(110) surface with 1/2ML of O$_{br}$ (red). The measured IP for H$_2$O in gas phase$^{38}$, the stoichiometric TiO$_2$(110) surface$^{25,38}$, the 6–9% hydroxylated $\overline{h}$–TiO$_2$(110) surface$^{25}$ and the liquid H$_2$O–TiO$_2$(110) interface$^{25}$ are shown in gray. The self-consistent OP GW $IP$ for H$_2$O in gas phase is indicated by the horizontal dashed lines. The experimental dielectric constant of bulk TiO$_2$, $\varepsilon_{\text{vac}} = 7.6$, averaged over the (110) surface is marked in red. A linear fit to the DFT IP (blue), and an exponential fit to the G$_0$W$_0$ IP (cyan) for H$_2$O in gas phase are provided for comparison.
For the H$_2$O–TiO$_2$ (110) interface, e.g., 1 ML intact H$_2$O@Ti$_{cur}$, the highest energy H$_2$O PDOS peak, $\epsilon_{PDOS}^p$, is pinned ~1 eV below the VBM across PBE DFT, HSE DFT, PBE scGW1, PBE $G_0W_0$, and HSE $G_0W_0$. For this reason, the IP of the H$_2$O interfacial levels is controlled by the alignment of the VBM with respect to the vacuum. This means we only need to consider the absolute VBM level alignment of the interface, i.e., the interface’s $\text{IP} = -\text{VBM} + E_{vac}$, as a descriptor of photoelectrocatalytic activity.

In Figure 11 we see that the IP of the interface follows a different ordering across the methodologies from that of gas phase H$_2$O. In particular, we find PBE $G_0W_0$ (6.0 eV) ~ PBE DFT < HSE06 $G_0W_0 \approx$ PBE scGW1 < HSE DFT (7.3 eV). Figure 12 shows that, as was the case for H$_2$O in gas phase, the IP of the H$_2$O@Ti$_{cur}$ interface across the various methods is ordered according to the method’s description of the screening, $\epsilon_{\infty}^{-1}$.

As discussed above, for hybrid xc-functionals such as HSE, the effective screening is determined by the fraction of exact exchange $\alpha$ included. Essentially, $\alpha$ plays the role of the effective screening within the method, $\epsilon_{\infty}^{-1}$. Although HSE06 incorporates less screening ($\epsilon_{\infty}^{-1}$) than for rutile TiO$_2$ ($\epsilon_{\infty}^{-1} = 7.6$, 55) the HSE06 IP for the interface is in agreement with the experimental estimate of $\text{IP} \approx 7.1$ eV $^{21,16}$.

If one performs $G_0W_0$ based on HSE06, a stronger screening is applied, i.e., $\epsilon_{\infty}^{-1} \approx 5.7$, yielding a lower IP for the interface. In fact, as indicated by the red arrow in Figure 12, a similar IP to HSE06 $G_0W_0$ should be obtained from HSE DFT by setting the fraction of exact exchange to the inverse dielectric constant of bulk TiO$_2$, i.e., $\alpha = 1/\epsilon_{\infty}^{-1}$. Adjusting $\alpha$ to the measured inverse dielectric constant has been previously found to give improved band gaps. From PBE scGW1, one obtains an IP consistent with that of HSE06 $G_0W_0$. This is because we see the screening in scGW decreases from PBE RPA with each self-consistent cycle. Essential, the final screening incorporated in scGW1 is similar to that of HSE06 RPA.

As shown in Figure 11, PBE $G_0W_0$ gives an IP slightly lower than PBE DFT for the interface, while the PBE $G_0W_0$ CBM is shifted up by about 2 eV. This is surprising, since PBE DFT already yields a CBM level alignment for the interface in excellent agreement with experiment. This is partially due to PBE RPA’s overestimation of the screening of TiO$_2$ ($\epsilon_{\infty}^{-1} \approx 8.3$). Although HSE06 $G_0W_0$ has a weaker screening than PBE $G_0W_0$, the resulting absolute alignment of the CBM is quite similar. If instead, the self energy corrections are applied self-consistently via PBE scGW1, the absolute alignment of the CBM is significantly lower, but still greater than that of PBE DFT or HSE06 DFT. This is again related to decreases in the dielectric constant with each self-consistent cycle. For this reason, scGW1 tends to provide reasonable band gaps for TiO$_2$(110) interfaces. Overall, we observe an ordering in increasing band gap of PBE DFT < HSE06 DFT < PBE scGW1 < PBE $G_0W_0$ = HSE06 $G_0W_0$, with HSE06 DFT providing the best absolute alignment of the CBM and VBM for the H$_2$O@Ti$_{cur}$ interface.

In Figure 12 we see that a similar correlation between IP and the method’s description of screening holds for clean and hydroxylated h–TiO$_2$(110). Specifically, we consider clean stoichiometric TiO$_2$(110) and dissociated H$_2$O@O$_{vac}$ on defective TiO$_2$–$_{\perp}$(110) with $\frac{1}{2}$ ML of O$_{vac}$. Overall, $\text{IP} = \text{IP}_{\text{PBE}} + 5.9\alpha$ for all systems considered. We again find that the IP of PBE $G_0W_0$ ~ PBE DFT, HSE06 $G_0W_0$ ~ HSE($\alpha^{-1} = \epsilon_{\infty}^{-1}$) ~ PBE scGW1, and PBE scQPGW ~ HSE06 scQPGW ~ HSE06 DFT.

HSE06 DFT provides the most accurate description of the IP of the clean and H$_2$O@Ti$_{cur}$ covered stoichiometric TiO$_2$(110) surfaces. Although the HSE06 DFT IP for H$_2$O@O$_{vac}$ is significantly lower than the one measured for h–TiO$_2$(110), in both cases, the IP is shifted to lower energies relative to the clean stoichiometric surface. Differences in the magnitude of the shifts are probably due to the differences in defect coverage between the experiment (6–9%$^{22}$) and the calculation (50%).

The similarity between HSE06 DFT and scQPGW based on either PBE or HSE06 for the clean TiO$_2$(110) surface$^{22}$ points to a similar screening from these two techniques. This also demonstrates the starting point independence of the scQPGW technique.

To summarize, although scQPGW provides accurate IPs, the band gap is greatly overestimated, as reported previously.$^{22,34,12}$ While scQPGW provides a more accurate band gap, it achieves only a qualitative description of the IP. HSE06 achieves a quantitative description of both the IP and band gap, but provides a poor description of the molecular level alignment relative to the VBM. However, since the highest occupied H$_2$O levels are significantly hybridized with the substrate, this is not a major drawback in this case. In general, for TiO$_2$(110), a more effective strategy is to combine the calculated IP from HSE06 with the occupied interfacial levels’ alignment from $G_0W_0$ or scQPGW1.

4. CONCLUSIONS

The level alignment prior to photo-irradiation is an important piece of the puzzle needed to get a complete atomistic picture of photocatalytic processes. Here we have shown that the complex UPS spectra for the H$_2$O–TiO$_2$ interface may be disentangled using QP $G_0W_0$ PDOS. We have firmly established the robustness of the QP $G_0W_0$ H$_2$O PDOS by: (1) demonstrating its xc-functional (PBE, LDA, vdW-DF, and HSE06) independence, (2) comparing to self-consistent QP GW techniques (scQPGW1), and (3) considering its dependence on surface coverage and dissociation. Altogether, these calculations provide an accurate interpretation of the complex UPS and MIES experiments$^{22,23,24}$ for the H$_2$O–TiO$_2$(110) interface, and provide accurate estimates of the highest H$_2$O occupied levels’ alignment relative to the VBM.

Our results provide two important pieces of the puzzle: (1) the molecular structure of the photocatalytic interface and (2) the molecular alignment of the doubly occupied levels near the VBM responsible for hole trapping prior to irradiation. To complete the picture, the molecular structure and level alignment in the presence of the photo-generated hole is also needed. Previous DFT studies using the hybrid HSE xc-functional have found a hole can be trapped at surface O 2$p_\pi$ levels of O$_{hr}$ and HO–Ti$_{cur}$ sites. However, the screening of such localized levels may not be well described by HSE, which tends to underbind localized interfacial levels.$^{25}$ This underbinding is corrected upon inclusion of many-body effects via QP $G_0W_0$. Having demonstrated the capability of $G_0W_0$ for the description of level alignment prior to irradiation, this work points the way forward via future QP $G_0W_0$ studies of level alignment for trapped hole levels.

ASSOCIATED CONTENT

$^3$ Supporting Information

Total energies and optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.
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