Core-Level Binding Energy Reveals Hydrogen Bonding Configurations of Water Adsorbed on TiO$_2$(110) Surface

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(Received 9 September 2020; accepted 3 December 2020; published 7 January 2021)

Using x-ray photoelectron spectroscopy of the oxygen 1s core level, the ratio between intact (D$_2$O) and dissociated (OD) water in the hydrated stoichiometric TiO$_2$(110) surface is determined at varying coverage and temperature. In the submonolayer regime, both the D$_2$O:OD ratio and the core-level binding energy of D$_2$O (ABE) decrease with temperature. The observed variations in ABE are shown with density functional theory to be governed crucially and solely by the local hydrogen bonding environment, revealing a generally applicable classification and details about adsorption motifs.

DOI: 10.1103/PhysRevLett.126.016102

How oxides wet has significant implications for materials science, (photo)catalysis, fuel cells, corrosion, and environmental remediation [1,2]. Most oxides are hydroxylated at room temperature and atmospheric vapor pressure. Wetting involving dissociation into adsorbed H and OH can be generated at perfect areas, edges, and defects [3–6]. The first water layer is particularly important, since it acts as a template for the growth of additional layers [7,8]. Among oxides, titanium dioxide (TiO$_2$) is an important material in the fields of photocatalysis, solar fuel cells, and self-cleaning coatings [3,4,9–12]. For molecular-level understanding of hydration of oxide surfaces, the rutile TiO$_2$(110) single crystal surface [3,4,12] is a carefully investigated model system. At ideal stoichiometry (denoted s-TiO$_2$), it is entirely composed of alternating fivefold coordinated Ti ions (Ti$_{5c}$) and twofold coordinated bridging oxygen ions (O$_b$). The dissociation on defect-free TiO$_2$(110) surface has been a controversial topic [13,14], but recent experimental and theoretical efforts are consistent with the fact that the first water layer on a defect-free surface is partially dissociated [15–21].

A comprehensive molecular mechanism for the formation of the first water layer on the s-TiO$_2$ surface is still lacking. However, scanning tunneling microscope (STM) studies of water adsorbed on a reduced surface (i.e., with O$_b$ vacancies) have revealed a clear propensity toward chain formation [22,23], and time lapse STM images have shown a temperature dependent diffusion along the Ti$_{5c}$ rows [24]. On a close to ideal s-TiO$_2$ surface, x-ray photoelectron spectroscopy (XPS) in conjunction with density functional theory (DFT) and Monte Carlo simulations show a coverage dependent OH and H$_2$O speciation, ranging from initial formation of stable hydroxyl pairs to predominantly molecular adsorption at increasing coverage [18]. A study combining molecular beam, STM, and ab initio molecular dynamics has shown that molecularly bound water is preferred over the surface-bound hydroxyls by only 0.035 eV [25]. In conclusion, kinetic effects can clearly determine how the water layer is formed.

In this Letter, we demonstrate how detailed analysis of O 1s XPS spectra reveals crucial information about the first water layer on the TiO$_2$(110) surface. The measurements are closely aligned with DFT based core-level binding energies (BE) to obtain a molecular-level understanding of the XPS signal for intact and dissociated water molecules in different hydrogen bonding configurations at various coverages. We show that XPS not only discloses the chemical state of adsorption but also probes the bonding...
configuration between the water molecules on the TiO$_2$(110) surface. Importantly, a general trend in the BE was discovered allowing for classification into three distinct classes of hydrogen donation and to determine their presence at different growth temperatures.

The photoemission measurements were performed at beam line D1011 at MAX-IV in Lund, Sweden, using a SES200 electron energy analyzer (SCIENTA) [26]. The O 1$s$ spectra were recorded in 60$^\circ$ off normal emission using 610 eV photons. The BE was referenced to the Fermi level of a Pt foil attached to the sample holder. The coverage is given in monolayers (ML, with 1 ML being the density of a Pt foil attached to the sample holder. The uptake series were conducted at three temperatures, 97, 160, and 210 K. The variation of the O BE was discovered allowing for classification into three distinct classes of hydrogen donation and to determine their presence at different growth temperatures.

Figure 1(b) shows O 1$s$ spectra at an uptake of 0.2 ML at 97 and 210 K, respectively, after background subtraction. Shown at the bottom for comparison is the O 1$s$ spectrum for the clean s-TiO$_2$ surface. A relative $\Delta$BE is defined with respect to the component from TiO$_2$. The curve fit of the spectrum (black line) for the clean surface is made using two components [red (strong) and gray (weak)] of which the weak feature is needed to capture the asymmetry of the peak toward the high BE side. This asymmetry is partly due to small amounts of OD left after the surface preparation ($\leq 0.03$ ML) [15]. Upon adsorption and partial dissociation of water, two additional components, corresponding to D$_2$O (blue) and OD (red), appear. We conclude that for 0.2 ML water, a higher degree of dissociation occurs at 210 K than at 97 K. Further, $\Delta$BE for the peak associated with D$_2$O is 0.25 eV lower for deposition at 210 K than at 97 K. The variation of the O 1$s$ BE of D$_2$O under different temperatures is central to learning about the adsorption and will be addressed comprehensively below. The partial overlap of the OD feature with the TiO$_2$ peak prohibits detailed analysis of the OD species.

Figure 2 shows the results of real-time O 1$s$ XPS measurements upon water adsorption on the s-TiO$_2$ surface. The uptake series were conducted at three temperatures (97, 160, and 210 K) keeping $3 \times 10^{-10}$ mbar D$_2$O pressure. The D$_2$O and OD coverages ($\Theta$) are derived from the curve fitting described above. We also include the total water uptake, obtained as $[\Theta(D_2O) + 0.5 \times \Theta(OD)]$ since D$_2$O dissociation results in two OD groups. The uptake rate in all three cases is $0.042 \pm 0.004$ ML/min. At 97 K, there

![FIG. 1. (a) Structural model and (b) O 1$s$ spectra for water molecules adsorbed on TiO$_2$(110) surface, at two different temperatures, 210 and 97 K, for an uptake of about 0.2 ML. The BE of O 1$s$ for the clean s-TiO$_2$ surface has been taken as reference.](image)

![FIG. 2. Real-time monitoring of coverage upon water adsorption on s-TiO$_2$ surface at three temperatures, 97, 160, and 210 K.](image)
is no limit in the D$_2$O uptake since bulk ice is stable in UHV at this temperature. Water dissociation is still observed and the maximum OD coverage is 0.28 ± 0.05 ML (reached at 0.9 ML uptake). At 160 K, the saturation water uptake is 1.4 ML, partitioned into 1.2 ML molecular and 0.2 ML dissociated water. At 1 ML uptake, the layer comprises 0.83 ± 0.05 ML D$_2$O and 0.35 ± 0.05 ML OD. Comparison to previous measurements at 210 K [18] shows a shift toward the intact form at the lower temperature.

Figure 3(a) presents the D$_2$O/OD ratio for each step in the growth series. All three series are characterized by a progressive increase of the D$_2$O/OD ratio as the coverage increases. Higher D$_2$O/OD ratios are apparent at lower temperature. The overall similar slopes in the submonolayer regime indicate that the reduced dissociation at lower temperature primarily stems from the behavior at very low coverage. The hydrogen-bonded configurations that form result from having a critical distance between dissociated water and a tendency for intact water to bond to already adsorbed species (nucleation versus aggregation) [18]. This effect can be expected to be more important at low coverage.

Our source of information regarding the water configurations formed is the O 1s BE of the D$_2$O species. A redshift is known to occur upon hydrogen network formation when aggregates form [7,38,39]. Specifically, the variations in the D$_2$O/OD ratio entail changes in the O 1s configuration, expected to translate into O 1s BE shifts. The O 1s peak of D$_2$O is well separated from the other two components, namely OD and TiO$_2$, and its BE can be determined to within ±30 meV when the coverage is > 0.1 ML. Figure 3(b) shows the ΔBE between the O 1s peaks of D$_2$O and TiO$_2$ as a function of total amount of adsorbed water. At 97 K, ΔBE starts at a value of 3.95 eV at 0.1 ML uptake, after which it decreases progressively down to 3.2 eV at 2 ML. At 160 K, ΔBE is first 3.92 eV and then drops sharply to 3.69 eV at about 0.2 ML. The ΔBE value then stays constant at 3.67 ± 0.02 eV from 0.2 to 1 ML. Uptakes > 1 ML lead to a decrease in ΔBE due to the formation of the second layer, leading to a more extended hydrogen bonding network. In contrast, at 210 K, ΔBE starts at a low value (3.56 eV), after which it drops even further (to 3.50 eV) at 0.3 ML and then increases slowly, reaching 3.66 eV at 1 ML, which is quite close to that observed at 160 K. Interestingly, comparable D$_2$O/OD partitioning (0.79 ML/0.42 ML at 210 K and 0.83 ML/0.36 ML at 160 K) suggests that the overlayer structure formed at 1 ML has to be very similar in these cases. Consequently, growth at 160 K and at 210 K follows different routes toward the same monolayer structure. We also note that a significantly lower monolayer ΔBE value is found at 97 K (3.52 eV). A feasible explanation is that, at this temperature, second layer water adsorbs prior to the completion of the first layer. An observation supporting this notion is that the O 1s intensity of the OD related component starts to decrease at this coverage (see Fig. 2), which can be due to surface attenuation from the second layer.

The most striking difference between the curves is the low ΔBE values in the sub-ML regime observed upon growth at 210 K. Generally, a decrease in the O 1s BE from water is expected upon the formation of hydrogen bonding networks. For water on the TiO$_2$(110) surface, aggregation within the first layer occurs by formation of 1D chains, with the expected result of a decrease in ΔBE as the first layer is formed, as observed at 97 and 160 K. For sub-ML coverage formed at 210 K, however, the ΔBE values are even lower than the value attained at 1 ML, which cannot simply be explained in terms of early formation of extended water aggregates. A critical property that differs growth at 210 K from growth at the two lower temperatures is the higher tendency for water dissociation at low coverage. As aggregates form molecular water will coordinate to hydroxyl groups formed by water dissociation [18]. The results in Fig. 3(b) therefore imply that the ΔBE value for water coordinated to hydroxyls is lower than the average ΔBE value of the full layer, which comprises of water bonded to water as well as hydroxyls.

The energetics of wetting of the s-TiO$_2$ surface has been studied earlier [18], but here we perform DFT calculations of both adsorption energies and O 1s core-level BEs to gain a microscopic understanding and insight into the hydrogen bonding motifs as well as to probe their influences on the XPS spectra. Figure 4(a) shows a representative example of 30% coverage of water molecules on TiO$_2$(110) surface in three different configurations, namely M → M → D, M → M → M, and M → D → M (left to right). The arrow (→) indicates the direction of a donating hydrogen bond. The results for the adsorption energy versus coverage, summarized in Fig. 4(b), suggest that for low coverages (< 50%), the configurations containing M → D are relatively more stable as compared to those with fully intact water molecules. However, the configurations containing D → M are least stable. Clearly, having a dissociated water molecule as a hydrogen bond donor (acceptor) is
three classes of intact water molecules with distinct influence on the BE. The accepting hydrogen bond (from X) between intact D$_2$O and TiO$_2$ surface for all adsorption models. To rationalize the ΔBE of the D$_2$O signal, we assess the influence of the local hydrogen bond environment (X → M → Y) for an intact water molecule (M), where as exemplified in Fig. 4(a), X and Y can be either empty (□), M, or D. The ΔBEs for different coverages and local environments are summarized in Table I. See Fig. S2 in Supplemental Material for the geometrical configurations and their classification [40]. The accepting hydrogen bond (from X) has little influence on the ΔBE. Hence, XPS essentially probes three classes of intact water molecules with distinct energetically unfavorable (favorable). Hence, for our models of higher coverages 50% and 100% in which rows are filled, the configurations with purely molecular water become energetically more favorable compared to those with a dissociated molecule.

We also calculated the ΔBE for D$_2$O on the s-TiO$_2$ surface for all adsorption models. To rationalize the ΔBE of the D$_2$O signal, we assess the influence of the local hydrogen bond environment (X → M → Y) for an intact water molecule (M), where as exemplified in Fig. 4(a), X and Y can be either empty (□), M, or D. The ΔBEs for different coverages and local environments are summarized in Table I. See Fig. S2 in Supplemental Material for the geometrical configurations and their classification [40]. The accepting hydrogen bond (from X) has little influence on the ΔBE. Hence, XPS essentially probes three classes of intact water molecules with distinct ΔBE; namely, (a) X → M → □, (b) X → M → M, and (c) X → M → D. It is clearly seen from Table I that the values of ΔBE can be grouped into the three classes mentioned above. The highest and lowest values for ΔBE are observed for configurations from classes (a) and (c), respectively, whereas the class (b) configurations yield intermediate values. Thus, these results clearly show that the acceptor (Y) plays an important role in determining the BE. The decreasing ΔBE can be explained by the enhanced stabilization of the core-ionized state due to the increasing electron rich hydrogen bond acceptors. In addition, the difference in O 1s BE for both the terminal and bridging hydroxyls is found to be small (about 0.18 eV), with the value of the former on the higher side. Moreover, the average O 1s BE of hydroxyls is about 2 eV smaller than for molecular water. For evaluation, we also derived O 1s BE for 30% coverage using the Z + 1 approximation with both a hybrid functional PBE0 [46] and PBE (see Supplemental Material [40]). The sensitivity in ΔBE to XC functional is very small.

Our results on adsorption energy and ΔBE clearly indicate that at 210 K, predominantly class (c) type configurations are formed at low coverage (0.1 to 0.4 ML). In this regime, the energetically favorable configuration is M → D which belongs to class (c) that exhibits the lowest range of ΔBE. From 0.4 to 1 ML, the increasing values of ΔBE and adsorption energy are consistent with formation of larger cluster sizes which comprise M → M configuration, belonging to class (b). At 97 and 160 K, however, the dissociation probability is lower and, consistently, the values of ΔBE suggest that environments of class (a) and class (b) dominate at low coverage. At monolayer coverage, the intermediate value of ΔBE is due to configurations containing predominantly class (b) with a small contribution of class (a) environments at both 160 and 210 K, whereas at 97 K it is likely that multilayer islands energetically preferred class (c) over class (a). That the uptake series at 160 and 210 K reach monolayer coverage through different routes can be

![Figure 4](https://example.com/figure4.png)

**FIG. 4.** (a) Top view of three possible geometric configurations (M → D, M → M, and D → M) for 30% coverage of water molecules on TiO$_2$(110). (b) Adsorption energy versus coverage.

| Class | Configuration | 10% | 20% | 30% | 40% | 50% | 100% | Range |
|-------|---------------|-----|-----|-----|-----|-----|------|-------|
| a     | X → M → □    | 4.07| 3.96| 3.96|     |     |      |       |
| a     | M → M → □    | 3.91| 3.92|     |     |      |       |       |
| a     | □ → M → □    | 3.97|     |     |     |      |       |       |
| b     | M → M → M    | 3.41|     |     | 3.40–3.61| 3.49–3.58| 3.45–3.51| 3.36–3.61|
| b     | D → M → M    |     |     |     | 3.34|      | 3.37  |       |
| b     | □ → M → M    | 3.36| 3.36–3.43| 3.36–3.39| 3.24|      | 3.16–3.17| 2.93–3.24|
| c     | M → M → D    | 3.11|     |     | 3.11–3.22| 3.24|      |       |
| c     | □ → M → D    | 2.93| 3.08|     |     |      |       |       |

*Table I.* Difference in BE of O 1s between intact D$_2$O and TiO$_2$, obtained from DFT based electronic structure calculations with the PBE functional, versus coverage for various hydrogen bonding configurations. The last column contains the overall range of ΔBE values obtained for the classes.
rationalized in terms of surface diffusion effects. Diffusion along the Ti$_{5c}$ rows at 210 K is more than 1000 times faster than at 160 K [24]. However, if the temperature is too low to permit appreciable diffusion along the Ti$_{5c}$ row, transient diffusion along the O$_{5}$ rows or on top of already adsorbed water can occur before the molecule adsorbs on a Ti$_{5c}$ site. The different kinetics involved in nucleation and aggregation can thus yield metastable low-coverage configurations at 160 K (and 97 K) analogous to the behavior found for water on anatase TiO$_2$(101) [47].

In conclusion, measurements and simulations of O 1s XPS for water on the stoichiometric TiO$_2$(110) surface allow for insight into the mechanism of formation of first water layer as well as the temperature dependent kinetics of intact (D$_2$O) and dissociated (OD) water as a function of coverage and temperature. The uptake series at 160 and 210 K reach monolayer coverage through different routes, with higher degree of dissociation at 210 K, associated with lower values of $\Delta$BE for intact water in the submonolayer regime. Palpable differences in $\Delta$BE versus coverage can be rationalized in terms of surface diffusion effects. Diffusion along the Ti$_{5c}$ rows or on top of already adsorbed water can occur before the molecule adsorbs on a Ti$_{5c}$ site. The above findings will lead to further advancement in molecular-level understanding of water.

This work was supported by the Swedish Research Council (VR Contract No. 2015-03956) and the Swedish energy agency (Contract No. 2017-006797). The calculations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC).

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