

Adsorption Bond Length for H₂O on TiO₂(110): A Key Parameter for Theoretical Understanding

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Scanned-energy mode photoelectron diffraction results show the adsorption site of molecular water on TiO₂(110) to be atop under-coordinated surface Ti atoms, confirming the results of total energy calculations and STM imaging. However, the Ti-O_{water} bond length is 2.21 ± 0.02 Å, much longer than Ti-O bond lengths in strongly chemisorbed species on this surface, but significantly shorter than found in most total energy calculations. The need for theory to describe this weak bond effectively may be a key factor in the controversial problem of understanding this important surface reaction system.

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Despite the widely perceived view that the interaction of water with rutile phase TiO₂(110) is perhaps the most important of all model oxide surface reactions [1,2], with the photochemical production of hydrogen from water at this surface being discovered more than 30 years ago [3], there remains considerable controversy over the proper theoretical treatment of this system. In particular, while experiments show a stable adsorbed phase of molecular water at low temperature and indicate that any dissociation at higher temperatures is only mediated by surface defects, most theoretical calculations [e.g., [4–11]] have suggested facile dissociation should occur on a defect-free surface, at least at low coverages. A few such calculations, however, have correctly predicted nondissociative adsorption [12–15], but these results remain controversial [e.g., [16,17]]. Here we present the first experimental quantitative structure determination of this system. Our results show qualitative agreement with theory in terms of the adsorption site, and of an adsorption Ti-O_{water} bond length much longer than other Ti-O bond lengths in this system, indicative of weaker bonding. However, in the few theoretical papers which quote this bond length the values are consistently longer (by up to 0.20 Å) than the experimental value, indicating an underestimate of the strength of the TiO₂-water bonding. Interestingly, in the one paper which predicts molecular adsorption and quotes the Ti-O_{water} bond length [12], the value is close (only 0.04 Å longer) to the experimental value, reinforcing the view that a correct description of the molecular bonding may lie at the heart of the problem of correctly describing this important surface reaction.

Although oxide surfaces generally are of considerable practical importance, particularly in heterogeneous catalysis in gaseous and aqueous environments, there is a dearth of quantitative structural information, yet surface structure determination provides key atomistic parameters to test theoretical understanding. Scanned-energy mode photoelectron diffraction (PhD) [18] is able to provide element-specific and chemical-state-specific local structural information for adsorbates on surfaces, through the

coherent interference of the directly emitted photoelectron wave field from an adsorbate atom core level, and components of the same wave field elastically scattered by surrounding (substrate) atoms. In addition to many applications of this method to metal and semiconductor surfaces, PhD studies of CO, NO, and NH₃ adsorption on NiO(100) [19] revealed very large discrepancies (up to 0.79 Å) between experimental and theoretical molecule-surface bond lengths in these systems, which has led to significant new efforts to improve current theory [20]. NiO, however, is known to be particularly challenging to describe well theoretically, with density functional theory (DFT) proving particularly ineffective. By contrast, TiO₂ is regarded as far more amenable to effective theoretical description, with a range of methods, including DFT, proving fruitful. In particular, the structure of coadsorbed formate (HCOO⁻) and hydroxyl (OH) species on TiO₂(110) produced by the reaction of the surface with formic acid (HCOOH), also investigated by the PhD technique, was found [21] to be in excellent agreement with published theory, with bond lengths agreeing to within 0.01 Å. Clearly, current theoretical methods describe these strong chemisorption systems well. However, molecular water adsorption on TiO₂ involves substantially weaker bonding, as reflected by the much longer molecule-surface bond length which we find in our investigation; in this case there is a very significant difference between the experimental and most of the theoretical bond length values which must reflect inadequacies in the theory to describe this weaker bonding with sufficient precision. The apparent failure to calculate the barrier to dissociation correctly may well be related to the same theoretical weakness.

The experiments reported here were conducted in an ultrahigh vacuum surface science end station equipped with typical facilities for sample cleaning, heating, and cooling. This instrument was installed on the UE56/2-PGM-2 beam line of BESSY II which comprises a 56 mm period undulator followed by a plane grating monochromator [22]. Different electron emission directions can be detected by rotating the sample about its

surface normal (to change the azimuthal angle) and about a vertical axis (to change the polar angle). Sample characterization *in situ* was achieved by LEED and by soft-x-ray photoelectron spectroscopy (SXPS), executed using an Omicron EA-125HR 125 mm mean radius hemispherical electrostatic analyzer, equipped with seven-channeltron parallel detection, which was mounted at a fixed angle of 60° to the incident x radiation in the same horizontal plane as that of the polarization vector of the radiation. A clean well-characterized rutile $\text{TiO}_2(110)$ surface was prepared by briefly bombarding with either Ar^+ or Ne^+ ions (500 eV), followed by annealing in UHV at approximately 830 K, which gave a sharp (1×1) LEED pattern and a Ti $2p$ photoemission spectrum showing only a very weak high kinetic energy shoulder most commonly attributed to the presence of surface nonstoichiometry due to oxygen vacancies. This surface was exposed to typically 10^{-6} mbar \cdot s of H_2O , at a partial pressure in the high 10^{-9} mbar range, with a sample temperature of 125 K, and then heated to ~ 230 K and held at 190–200 K during measurement of the PhD spectra to ensure any multilayer water from the initial deposition was desorbed, and to prevent readsorption from the residual vacuum. No evidence of radiation damage, particularly partial dissociation of the water to form surface hydroxyl species, was seen in the experiments. In the case of hydrogen-bonded water bilayers on Ru(0001) on Pt(111), unlike water on $\text{TiO}_2(110)$, the possibility of observing experimentally partial dissociation to a mixed H_2O and OH layer has proved controversial [23,24], and in the former case, at least, there is clear evidence reported of radiation-induced dissociation during O $1s$ photoemission [23]. However, in our experiments the photon beam was defocused to ~ 1 mm² to minimize this problem. Relative to the study of water on Ru(0001) [23], conducted on a beam line with $10\times$ higher total flux and a $6 \mu\text{m} \times 11 \mu\text{m}$ spot size, our photon flux density at the surface is approximately 10^4 – 10^5 times lower ($\sim 5 \times 10^{11}$ photons mm⁻²) and our data collection times for the PhD spectra (~ 1 hour) are thus consistent with a smaller integrated number of incident photons per unit area than that found to give no significant radiation damage (in ~ 3 s) in the Ru study.

Figure 1 shows the O $1s$ SXPS spectrum associated with low temperature water dosing and subsequent annealing. The feature with a chemical shift of ~ 3.5 eV relative to the oxide peak is attributed to adsorbed molecular water on the surface, the energy differing slightly between the initial adsorbed multilayer and the annealed single layer. No evidence was seen after heating to room temperature of a shoulder on the oxide O $1s$ peak with a smaller chemical shift of about 1.6 eV, attributed to OH on the surface due to water dissociation [25]. The PhD modulation spectra were obtained by recording a sequence of photoelectron energy distribution curves (EDCs) around the O $1s$ peaks at 4 eV steps in photon energy in the photoelectron kinetic energy

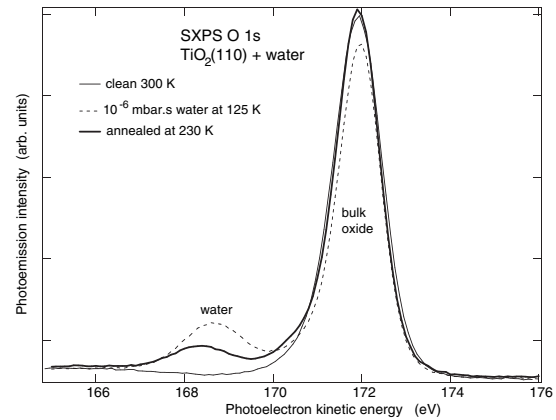


FIG. 1. Soft x-ray photoelectron spectra in the energy range of the O $1s$ emission recorded at a photon energy of 700 eV from a clean $\text{TiO}_2(110)$ surface, and from the same surface following low temperature exposure to water and subsequent heating. The two main component peaks due to emission from the TiO_2 substrate, and from the adsorbed water, are labeled.

range of approximately 50–315 eV. Fitting each of these spectra to a background and two Gaussian peaks, one from the oxide and one from the adsorbed water, allowed normalized PhD modulation spectra from the O atoms of the adsorbed water to be extracted. The correct shape for the background is determined from the “tails” of the individual EDCs measured at different photon energies. A second fitting routine, also applied to the raw data, included an intermediate third Gaussian peak at the O $1s$ binding energy corresponding to coadsorbed OH, but the PhD modulation spectra extracted from the molecular water component of the O $1s$ emission was essentially identical in these two different approaches. The PhD modulation spectra obtained from the intermediate feature in the three-peak fit was found to be similar to that from the oxide peak, suggesting that any possible shoulder at this binding energy is not due to coadsorbed hydroxyl but is directly related to oxide O atom emission. Most importantly, we conclude that the PhD spectra used in the present analysis correspond only to adsorbed molecular water. A set of 10 such PhD spectra, recorded in different emission directions, was used for the structural analysis, conducted through the use of multiple scattering simulations with computer codes developed by Fritzsche [26–28]. The fit between the experimental spectra and the theoretical simulations for a series of model structures was optimized with the aid of a reliability factor or R factor, based on a normalized sum of mean-square deviations, the final structural precision being defined by a variance as described elsewhere [29]. The structural parameters describing the position of the O atoms of the water molecule, the surface relaxations of the TiO_2 , and the vibrational amplitudes were searched on an extensive multidimensional grid. The results of this analysis led a lowest R -factor value of 0.150, consistent with the generally good fit to experiment

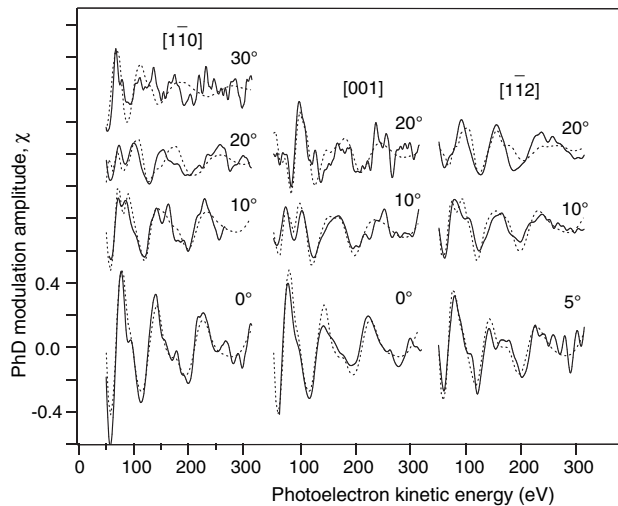


FIG. 2. Comparison of the full set of experimental O 1s PhD spectra (full lines) from adsorbed H₂O on TiO₂(110) used in the structural optimization, with the results of the calculations (dashed lines) for the best-fit surface geometry.

shown in Fig. 2; the PhD modulations are reasonably strong, particularly at normal emission (up to $\pm 40\%$ —see Fig. 2) so a low R factor is expected for the correct structure.

The adsorption site found in this analysis is atop the fivefold coordinated (i.e., under-coordinated) Ti surface atoms (Fig. 3), consistent with the results of theoretical total energy calculations and the interpretation of STM images [13,30]. The parameter of greatest importance in the PhD analysis is the Ti-O_{water} bond length which was found to be 2.21 ± 0.02 Å; this value was almost completely insensitive to alternative models of the surface

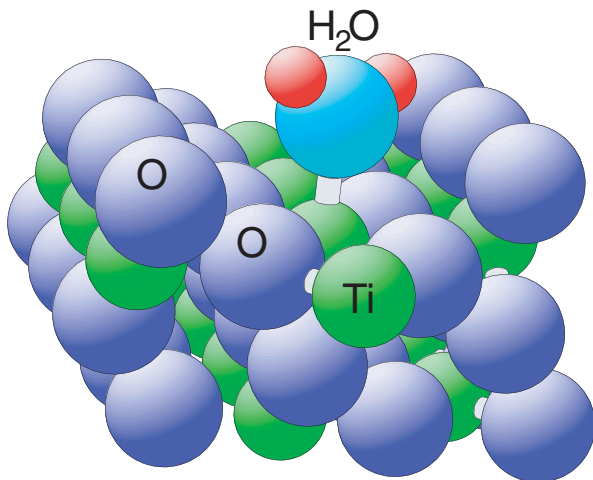


FIG. 3 (color online). Schematic view of the local adsorption site for H₂O on TiO₂(110) atop the fivefold coordinated Ti atoms of the surface. The H atoms within the H₂O molecule are included for illustration only; their location is not known from this study.

relaxation. Particularly for atop adsorption sites, a dominant sensitivity to this nearest-neighbor scattering distance is typical of the local character of the PhD technique. This Ti-O bond length is very significantly longer than that associated with the chemisorption bonds of formate (2.08 Å) and hydroxyl (2.02 Å) on this surface, and with the Ti-O bond lengths in the bulk oxide (1.94 Å and 1.99 Å), and clearly reflects a weaker bonding of a different character for the intact water molecule.

Despite the many theoretical papers reporting investigations of the adsorption and dissociation of water on TiO₂(110), very few of these papers record adsorption bond lengths; there appears to be just four such reported values for the Ti-O_{water} distance, namely, 2.25 Å [12], 2.28 Å [9], 2.32 Å [10], and 2.41 Å [31], all larger than the experimental value by more than the estimated experimental errors. However, the embedded cluster calculation giving the smallest value of 2.25 Å [12], rather close to the experimental value, was the one calculation of these four which specifically claimed to identify this as a stable molecular species relative to dissociation. In the DFT slab calculation of Zhang and Lindan [8], which found a value of 2.32 Å for the pure water layer, further calculations were also performed for a surface having coadsorbed water and oxygen, and in this case a shorter Ti-O_{water} bond length of 2.27 Å was found; associated with this shorter bond length was a stronger surface bond.

The details of the arguments in the literature concerning the merits and problems of different theoretical and computational methods, and the reasons why most theoretical calculations have incorrectly identified facile water dissociation on TiO₂(110), are beyond the scope of this Letter. However, in discussing these computational and theoretical problems, there has been an absence of any atomic-scale quantitative experimental data with which to confront the calculations. It is probably for this reason that so few theoretical papers have actually reported values for interatomic bond lengths, despite the fact that they must have been calculated in most cases; instead, these papers focus only on the existence, or otherwise, of significant energy barriers to dissociation. Our new results not only provide a value for the adsorption bond length, but also show that, where comparisons are possible, most current theories are failing to correctly reproduce this parameter. The one notable exception is the only calculation [12] which also predicts stable molecular adsorption. One obvious question is whether those more recent calculations which correctly identify molecular adsorption as the stable state also yield Ti-O_{water} bond lengths in reasonable agreement with the experimental value; this should be an important criterion in the debate as to the correct way to describe this system theoretically. Of course, whether or not water dissociation occurs on this surface depends not only on the equilibrium state of the weakly adsorbed molecule, and of the strongly adsorbed fragments, but also on the various possible tran-

sition states. However, it seems reasonable to suppose that the limitations which may lead to a poor description of the molecular adsorption state will also impact on the proper description of the transition states of the water molecule on TiO_2 . As such, achieving a good description of the molecular adsorption may also be a key to a more consistent description of the whole surface reaction.

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