Exothermic water dissociation on the rutile TiO$_2$(110) surface

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There has been a long-running debate among theorists and experimentalists on the precise nature of water adsorption at the TiO$_2$(110) surface. Some experimentalists argue that dissociative adsorption occurs only at defect sites (O vacancies) and therefore at low coverages. Although there is no doubt that vacancies are strongly reactive, until now there has been no firm understanding of adsorption on a perfect surface with which to contrast behavior. Here we report extensive and very detailed calculations that demonstrate that dissociation of a molecule is exothermic. Experimental findings are rationalized by the existence of a metastable molecular state separated from the dissociated state by a substantial barrier. We show that the barrier varies in height with coverage and with the presence of neighboring adsorbates, and we detail mechanisms for both phenomena. Finally, we reassess photoelectron spectroscopy results, showing their consistency with our predictions.

I. INTRODUCTION

The adsorption of water molecules on the rutile TiO$_2$(110) surface has received more attention than any other comparable system.[1–6] Water is celebrated for its intriguing properties and ubiquity in interfacial systems, making it an important and interesting surface science probe.[5] On the TiO$_2$(110) surface its behavior remains highly controversial. Understanding water adsorption has proved to be far harder than might have been imagined, and theorists and experimentalists still have not reached a consensus on one of the most basic and important questions: does water dissociate upon adsorption? We must know the state of adsorbates in order to argue sensibly about other matters, such as surface reactivity, the nature of adsorption complexes, or the properties of the oxide-solution interface. We must know the *fundamentals* of the process because of their importance in advancing the science of oxide surface chemistry. That a substantial number of experiments are at odds with theory points at either deficiencies in one or both, or a failure to understand the essential ingredients of the problem. This explains why such importance has been attached to understanding this system and why it is being probed so vigorously.

Using vacuum surface science methods, experimentalists have struggled to find evidence for low-coverage dissociative adsorption on the defect-free (110) surface. Henderson's view, which is probably the majority view, is that at all coverages water adsorbs molecularly and only dissociates at defect sites (particularly O vacancies) (Ref. 2) and therefore at coverages of 0.25 monolayer (ML) or lower. Some earlier studies suggested that adsorption occurs dissociatively at low coverages and thereafter molecularly[7] or either molecularly or dissociatively depending on temperature.[8] For a long time theory was in complete contradiction, saying that water dissociates at all coverages.[9–14] We have shown recently that intermolecular hydrogen bonding plays a role in determining adsorption state.[15] Specifically, we found that a mixed adsorption state was the most favorable at 1 ML, consisting of alternating molecular and dissociated forms running along the [001] rows of titanium fivefold-coordinated ions (see Fig.

1 of Ref. 15 for a diagram of the surface). We argued that this stabilization of the molecular form within an adsorbate pair may go some way towards explaining the experimental situation at lower coverage. However, we were still left with no firm conclusion from theory about the state of single molecules at low coverages on the defect-free surface. Schaub *et al.*[4] have used scanning tunneling microscope (STM) measurements and first-principles calculations to argue for water dissociation *exclusively* at oxygen vacancy sites and to rule out dissociation on the defect-free surface. Part of their justification was that they calculated dissociation to be *endothermic* at 0.25 ML and around 0.79 eV/molecule less favorable than molecular adsorption. Dynamical calculations by Langel,[16] in which he observed recombination of dissociation fragments, appear at face value to lend support to this view.

Here we present first-principles calculations designed with the aim of settling two arguments. First, what are the calculated energetics of water adsorption? Contrary to first appearances this is still an open question since (a) the energetics vary considerably with coverage and (b) previous calculations are subject to some degree of uncertainty. We have looked at a wide range of coverages and taken great care with computational errors to produce highly converged results showing that dissociation of a single H$_2$O molecule is always thermodynamically favorable, the distinction being highly marginal at 0.5 ML. Where we disagree with previous calculations[4,16,17] we explain why there are discrepancies and why we think our results are more reliable. Second, why do experiments fail to see dissociation? We show that a metastable molecular state is separated from the dissociated state by quite a high barrier at low coverage, but the height of the barrier depends on the coverage *and* presence of neighboring adsorbates. The net result is that the coverage and temperature must both be fairly high if dissociation is to occur. A large part of the answer therefore is that dissociation is kinetically hindered, but we also show that photoelectron spectroscopy (PES) will struggle to differentiate between dissociation on the perfect surface and dissociation at oxygen vacancy sites. What emerges from this work is a significant

extension of the theory and a coherent interpretation of experiments.

II. TECHNICAL DETAILS

The plane-wave pseudopotential density-functional-theory (DFT) techniques we use[18] are well established and validated, and have been reviewed extensively.[19–22] They have been validated in studies of TiO_2 bulk[23] and surface[24,25] properties and surface reconstructions.[26,27] They have proved particularly valuable in the study of water chemistry at oxide surfaces.[13–15,28–32] Our current theoretical understanding of low-coverage water adsorption on rutile (110) is summarized in Refs. 3, 15, and 33.

The main geometric features of the rutile $TiO_2(110)$ surface are fivefold-coordinated Ti ions and bridging oxygen ions. Water binds strongly to the fivefold Ti ions, and up to 1 ML adsorption is expected to be at these sites.[14,15,34] In order to probe how adsorption changes with coverage we have performed calculations on a range of systems extended along $[001]$ and $[1\bar{1}0]$; the surface unit cells employed ranged from 1×1 to 4×1 and 2×2. Two families of calculations were performed: one with a single adsorbate per surface, the other with pairs of adsorbates on a surface. Within each set we explored possible combinations of molecular and dissociated adsorbates. The systems studied are illustrated schematically in Fig. 1. We used slabs consisting of five O—Ti-O-Ti-O—O layers (except where we explore system size effects), and adsorbates were placed on both sides of the slab. Both of these are essential features in achieving good convergence of adsorption energies: values calculated with three-layer slabs are likely to be in error by around 30–40% as will be shown, and single-sided adsorption calculations converge more slowly than two-sided ones.[35] The error in the difference of two adsorption energies is no more than a few hundredths of an eV with a five-layer model, but it grows to ~0.3 eV for a three-layer model. We emphasize these points because for this combination of techniques and materials, limited system size is the first-order source of error in adsorption energies. Ultrasoft pseudopotentials were used with Ti 3p semicore states treated as valence, a 340 eV cutoff was applied to the plane-wave expansion, and a vacuum gap of 10 Å was used, choices explained in previous related work.[33] The maximum **k**-point spacing was no greater than 0.05 Å^{-1}. Exchange and correlation were treated via the revised PBE functional,[36] an important choice since hydrogen bonding exerts a crucial influence on the adsorption state, as will be seen later. Adsorption energetics were calculated from fully relaxed systems in which no ionic force exceeded 0.03 eV Å^{-1}. The adsorption energy is defined as $E_a = (E_s + nE_{H_2O}) - E_{sys}$ where E_s is the energy of the clean relaxed surface, E_{H_2O} that of a gas-phase water molecule, and E_{sys} that of the relaxed system, with the auxiliary energies computed so as to maximize error cancellation.

III. RESULTS AND DISCUSSION

A. Energetics

The calculated adsorption energies are summarized in Table I. We start our discussion with the single-molecule results in the series $(n \times 1)$, discounting the (1×1) system where the molecules are close enough to benefit from hydrogen bonding. All adsorption states are exothermic, and it can be seen that the dissociated state (DS) is favored over the molecular state (MS) in all cases, although the energy difference is marginal in the (2×1) or half-ML case. To test this marginal case we increased the slab thickness to seven layers; the relative stability remains the same, although the absolute energies decrease somewhat. A striking trend is that the amount by which dissociation is favored increases with decreasing coverage, ranging from 0.02 eV at 0.5 ML to 0.19 eV at 0.25 ML. For the (2×2) system, the same as was used in Ref. 4, dissociated H_2O is 0.2 eV more strongly bound than molecular H_2O. This is at odds with the results in Ref. 4 which give 0.56 and −0.23 eV for the MS and DS, respectively, compared with our 0.36 and 0.56 eV. Such a large discrepancy needs investigation, especially since the results in Ref. 4 are used by those authors in part justification of their conclusions. To this end we have replicated the methods they used, including a three-layer slab, the same **k**-point sampling, the use of the PW91 functional for geometry minimization, and *post hoc* application of the RPBE functional. This procedure yields 0.63 eV (MS) and 1.08 eV (DS), and we have to conclude that there is no obvious way to reproduce the DS energy reported by Schaub *et al.* For all systems considered here, we conclude that the dissociation of a single molecule is always exothermic and always favorable to molecular adsorption.

We digress briefly to consider a technical point. It is a well-established idea that, when considering adsorption of water at certain oxide surfaces, particularly those of titania, interadsorbate hydrogen bonds are a crucial ingredient in the balance of energetic terms.[15,30–32] There is a wide variation in the performance of different functionals in describing hydrogen bond energetics, making the choice of functional a crucial one. The minimum requirement is that gradient corrections be included,[37] but even then the choice is wide and the potential problems considerable. The Becke exchange-only generalized gradient approximation (GGA) (or *B* functional), for example, underestimates the water dimer binding energy by almost 50%,[37] which is the primary reason why some studies fail to observe water dissociation on $TiO_2(110)$ under any circumstance.[16] This shortcoming shows up in bulk water too, where the radial distribution function is understructured due to the weak H bonds. Addition of the Perdew gradient corrections for correlation (yielding BP) produces H bonds a little too strong and bulk water a little too structured. The functional we have used, the RPBE, gives rather accurate predictions of the binding energies of the dimer and small clusters, slightly underestimating the values.

Returning to the results, the two-H_2O-molecule energetics reveal that, as expected, the interadsorbate interactions have an influence. A general point is that, with a neighbor adsorbate, the binding energy is enhanced at given coverage. This is true in a like-for-like comparison, e.g., MS (one H_2O molecule) versus MS (two H_2O molecule), but more pronounced when the more strongly adsorbing mixed states are considered. At 0.5 ML the two-H_2O-molecule (4×1) mixed state is 0.12 eV/molecule more exothermic than the one-H_2O-
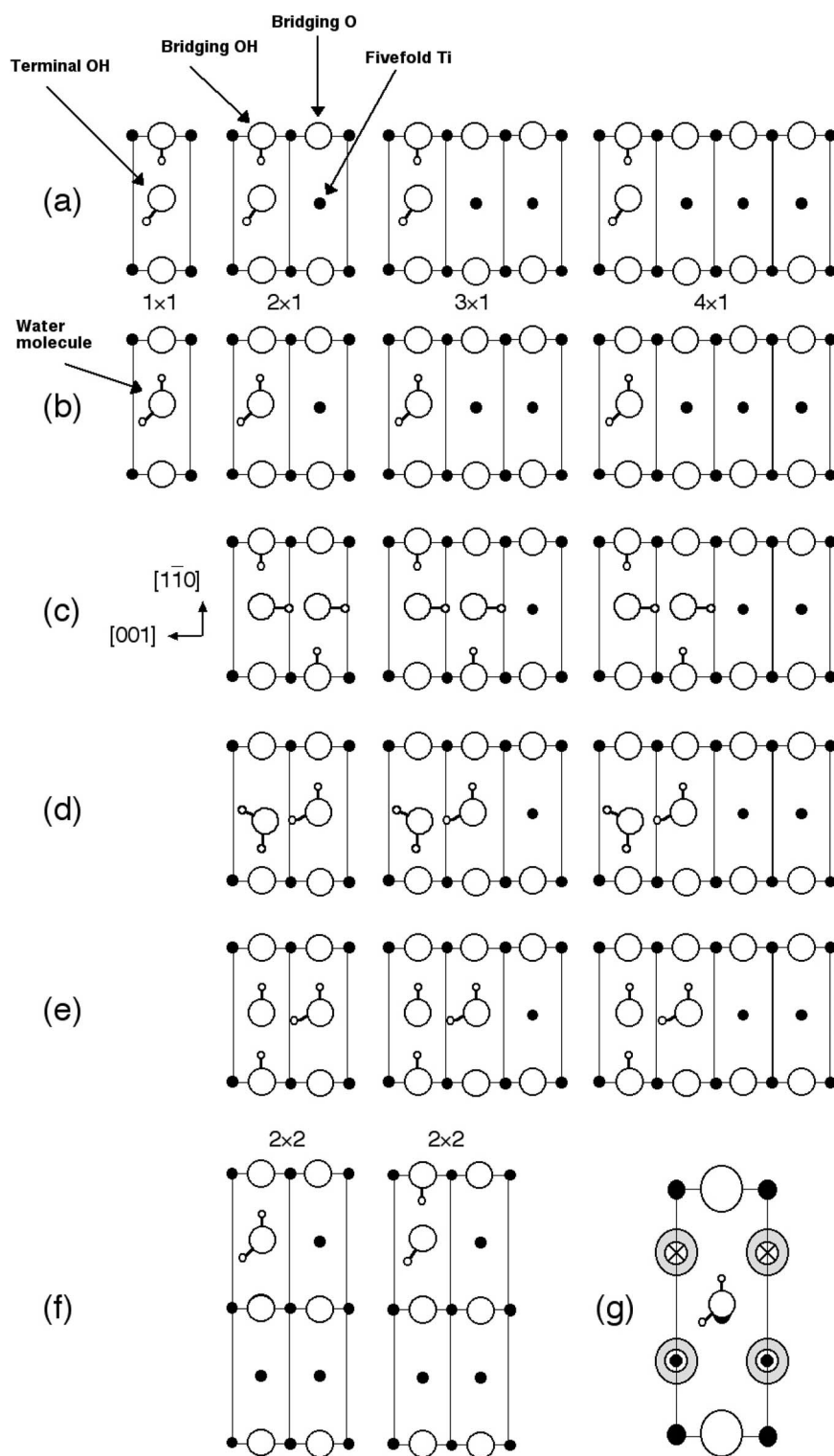
FIG. 1. Schematic representation of model systems. Ions are depicted as large open circles (oxygen), small open circles (hydrogen), and solid circles (titanium). The labeling is discussed in the text. (a), (b) Single-H_2O dissociative and molecular adsorption respectively. (c), (d), (e) The all-OH, all molecular, and mixed geometries for two-H_2O adsorption. (f) Molecular and dissociative adsorption on a 2×2 substrate. (g) In-plane oxygen ions (gray) and their motion into and out of the plane, discussed in the text.

molecule (2×1) dissociated state. Even the 1-ML DS state benefits from slight symmetry breaking induced by the interaction to increase the adsorption energy to 0.31 eV. The most important conclusion is that at lower coverages the presence of neighbor adsorbates still results in the most favorable state being one containing dissociated water (the mixed state). At ML coverage there is no numerically significant difference in the adsorption energy of MS and mixed

states. Moving to a seven-layer slab suggests that the mixed state is marginally favored.

B. Dissociation barriers

We have shown that dissociative adsorption is energetically favorable at low coverages for a single H_2O; consideration of H_2O pairs shows that the favored state contains mo-

TABLE I. Adsorption energies per H_2O as a function of coverage. The labels MS, DS, and Mix denote molecular, dissociated, and mixed adsorption states, respectively.

Unit cell	One H_2O		Two H_2O		
	MS	DS	MS	DS	Mix
(1×1)	0.51	0.28	—	—	—
(2×1)	0.48	0.50	0.54	0.31	0.54
(2×1)[a]	(0.40)	(0.42)	(0.52)	(0.34)	(0.53)
(3×1)	0.40	0.53	0.46	0.46	0.57
(4×1)	0.49	0.68	0.54	0.55	0.62
(2×2)	0.36	0.56	—	—	—
(2×2)[b]	(0.63)	(1.08)	—	—	—

[a]Calculated using seven-layer slabs.
[b]Calculated using three-layer slabs.

lecular and dissociated water at all but full ML coverage. This leaves an apparent discrepancy with experiment, and two obvious questions are whether the dissociated states are accessible under experimental conditions and whether the experiments themselves are able to distinguish between the different adsorption states. To answer the first question we have calculated the barrier to dissociation, using a constraint-based method described elsewhere.[38,39] We define the barrier height as the difference in system energy between the transition state and the initial molecular state, the latter being the state with both H_2O in molecular form when looking at two-H_2O-molecule systems. The results of these calculations are presented in Table II.

The two important features of the single-H_2O-molecule results are the rather large barrier at the lowest coverage and the trend for the barrier to increase with decreasing coverage. We shall explain the latter shortly, but dealing with the observation first, we can immediately see that at "low" coverages—say, 0.1 ML—we should predict a substantial barrier to dissociation. It must be remembered too that DFT-GGA calculations are almost certain to underestimate the barrier height.[40] This is a significant result, because the usual

TABLE II. Calculated energy barriers to dissociation, E_B. Also shown are the H-BO distances in the initial state (IS). The parameter d is a measure of the substrate deformation in the IS and the transition state (TS), and is explained in the text.

Unit cell	E_B (eV)	H-BO IS (Å)	d IS (Å)	d TS (Å)
One H_2O molecule				
(1×1)	0.25	1.960	0.189	0.420
(2×1)	0.36	2.067	0.173	0.251
(3×1)	0.33	2.100	0.164	0.239
(4×1)	0.45	2.121	0.155	0.258
Two H_2O molecules				
(2×1)	0.26	1.994	0.121	0.185
(4×1)	0.28	2.050	0.141	0.201

experimental procedure is to dose the surface at low temperature, around 100 K.[7] We should, therefore, predict that water adsorbed at low temperature would remain in molecular form, since the barrier to dissociation implies very slow kinetics. A simple analysis[41] shows that if the barrier were 0.5 eV, there would be very little thermal dissociation of molecular water over a time scale of a few hours; a higher barrier of, say, 0.7 eV, which is quite plausible given the trend and probable underestimation, would essentially inhibit all dissociation.

We must sound a note of caution with the foregoing argument. We have not considered the details of the adsorption process itself and, in particular, the potential influence of thermalization rate and steering. The adsorption energy at low coverage ($\sim$0.4 eV) is of the same order as the barrier we expect to exist ($\sim$0.7 eV). Clearly this could increase the likelihood of direct dissociation while the system is out of equilibrium. The adsorption energy released must be thermalized rapidly enough to avoid substantial direct dissociation. That the adsorption energy is lower than the barrier by a good margin gives reason to think this will be true, but the greater justification comes from the certainty that experiment sees molecular adsorption at low T combined with our clear result showing energetically favored dissociation: the most plausible explanation is that the barrier is sufficient to prevent dissociation. We also do not know whether molecules are steered into geometries that favor or disfavor dissociation. The latter would of course provide more time for thermalization to occur. These are substantial topics where further work is required.

The results also reveal that the barrier to dissociation is lowered if the dissociating H_2O is H bound to a neighboring molecule. To see this, the comparison to make is that of the single H_2O in the (2×1) cell with the two-H_2O-molecule (4×1) system. The coverage is the same in both cases, but the barrier is lowered from 0.45 eV to 0.28 eV. A similar effect seen in calculations on the anatase (101) surface has been reported recently.[32] This neighbor-induced lowering suggests another factor connecting dissociation and coverage. At low coverage, any given adsorbate would be unlikely to have neighbors, as long as the mobility of the adsorbates is low. Water becomes mobile at around 160 K,[4] so this neighbor-induced barrier lowering is only relevant at that temperature and above. However, in that regime the barrier lowering suggests that water "chains" that form along [001] will contain some dissociated H_2O. Recently we have discussed at some length the energetics of these chains and the consequences for TPD (Ref. 33), we note in passing that they, along with the trend to higher adsorption energies at lower coverage for isolated H_2O, are responsible for the broad TPD peak observed for first-layer desorption. In fact, some experimental work has indicated that some dissociation occurs in the first ML upon heating above 160 K.[8] While mobile H_2O could certainly find oxygen vacancies upon which to dissociate,[4] it could also find other adsorbates and thence benefit from the barrier lowering we predict from our calculations.

C. Barrier height coverage dependence

We turn now to the question of why, for a single adsorbate, the barrier to dissociation increases with decreasing
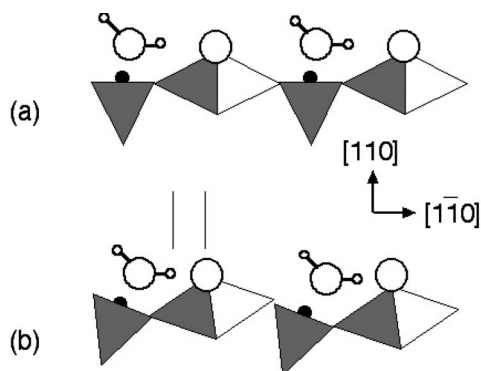
FIG. 2. Schematic representation of rigid-unit substrate deformation. For simplicity the only ions shown explicitly are fivefold Ti, bridging oxygen, and those of molecular water; an oxygen ion is at each octahedron vertex and a titanium ion at each center. (a) Unrelaxed geometry, (b) after relaxation. The displacements are greatly exaggerated for clarity. In (b) the H-BO distance is indicated.

coverage. We can go some way towards explaining this interesting behavior by considering how the substrate responds to the adsorbate. When water adsorbs on the fivefold-Ti-ion surface site, it also binds to the nearest bridging O ion, and this sets up a stress whose release draws together the fivefold Ti and bridging O ions. A measure of the strain is the H-BO distance, which we report in Table II. Part of the lattice strain is due to displacement along the eigenvector of a so-called rigid-unit mode (RUM): rutile may be viewed as a lattice of octahedra (the rigid units) sharing edges and corners, and rotation of the octahedra relative to each other is particularly easy in such a mode. This is illustrated schematically in Fig. 2. We must stress that this motion is not that of a pure bulk mode; it occurs at the surface, and the amplitude rapidly decays inside the slab.

Note that the force activating the mode is proportional to the number of adsorbates per unit length along [001]. It is reasonable to expect that the lower the coverage, the smaller will be the amplitude of the mode, assuming the strength of the surface-adsorbate interactions remains the same. As a measure of this kind of deformation we use the relative positions of the in-plane oxygen ions. These are indicated in Fig. 1(g). Because of the RUM strain, the in-plane O ions move into or out of the plane; in the figure, the lower pair of ions move out and the upper pair move in, indicated with an obvious notation. The degree of rotation of the octahedron is small enough to allow the use of the difference in vertical height, denoted as d, as our measure. This is reported in Table II for both the initial state and the transition state.

As can be seen, there is a correlation between the dissociation barrier and the H-BO separation. This is to be expected and has been invoked previously[42] in the interpretation of the differences between adsorption at the (110) and (100) surfaces. What is new here is the demonstration that the separation depends upon coverage, and hence the barrier depends upon coverage. Moreover, the connection with the RUM distortion is in evidence through the variation of d with coverage. In the initial state it is clear that as coverage drops, the reduced number density of adsorbates results in
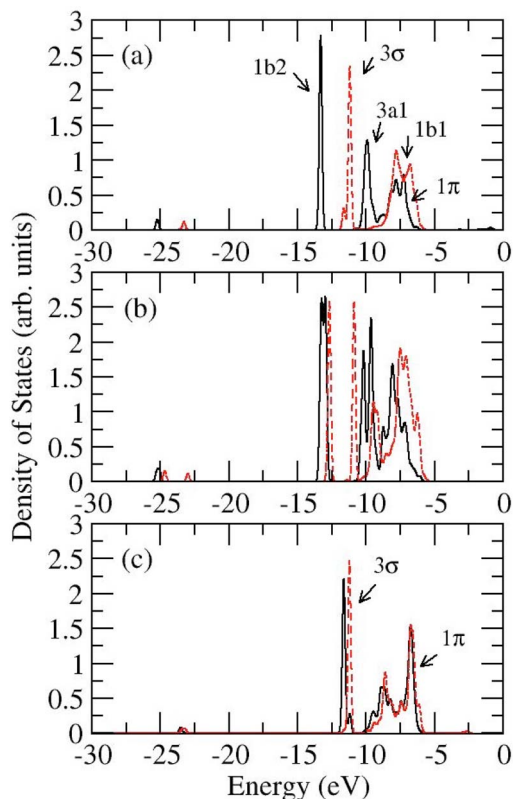

FIG. 3. (Color online) Projected densities of states, all for a (2 ×1) surface cell: (a) projection onto water O in MS (solid line) and DS (dashed line), one H_2O molecule in the cell; (b) projection onto water O in MS (solid line) and Mix (dashed line), two H_2O molecules in the cell; (c) projection onto BO in DS on the perfect surface (solid line) and surface with an O vacancy (dashed line), one H_2O in the cell.

less and less deformation. The involvement of the RUM distortion in the dissociation barrier is shown clearly by the d values in the transition state, which are around 1.5–2 times greater than those in the initial state. We note that the relationships are not exactly linear—e.g., in the variation of E_B with coverage. This has a similar origin to that of the well-known oscillation of surface properties with slab thickness in this system.[33,43,44] Basically, odd (even) numbers of layers in the slab permit a lesser (greater) degree of flexure, leading to oscillatory convergence of properties. This is a technical nuisance when converging surface calculations, as we have noted above. The nonlinear variation of E_B here though is somewhat different. The substrate deformation is not a pure RUM, since along [001] we alternate between odd and even numbers of vacant Ti sites as the coverage changes: different combinations of surface modes arise for odd and even cases. These would be present for any slab thickness. Finally, in this section, we note that the trend with coverage is only established in the single-H_2O-molecule results. With two adsorbates we have not accessed a system large enough to reveal the trend, our limit being half-ML coverage. It is interesting though to observe the lesser degree of deformation in both initial and final states, compared with the one-H_2O-molecule values. This tells us that the substrate effects, so important to a single adsorbate dissociation barrier, exert a

weaker influence on a pair of adsorbates. This is a factor that contributes to the neighbor-induced lowering of the dissociation barrier.

D. Partial density of states and photoelectron spectroscopy

We conclude this section by presenting calculated projected densities of states (PDOS), shown in Fig. 3. These can be used to understand PES spectra. Two PES studies[45,46] found 3σ and 1π contributions to be absent from spectra taken from water-dosed surfaces at low temperature. These signals are characteristic of the dissociated species, and hence those authors concluded that low-temperature adsorption was molecular. Heating to ~290 K leads to PES spectra with the features present. The dissociation this signals was assumed to occur at O vacancy sites.[45]

Our calculations confirm, as expected, that the 3σ and 1π features are characteristic of dissociated H_2O. Figure 3(a) shows this for a single H_2O molecule in the (2×1) cell. However, they also show that PES sees no difference between dissociation at a defect and dissociation on a perfect surface. Figure 3(c) shows that the PDOS and, hence, PES spectra, for the dissociated state on the perfect surface and at a bridging oxygen vacancy site, are basically indistinguishable. The mixed state at monolayer coverage, Fig. 3(b), shows characteristics of both molecular and dissociated forms, as might be expected.

IV. CONCLUSIONS

We have shown that well-converged DFT calculations predict that dissociated water is more strongly bound to rutile $TiO_2(110)$ than molecular water over a range of coverages, marginally so at 0.5 ML in a 2×1 cell and substantially so at lower coverages. We can reconcile this with experiments performed below 160 K that find only molecular adsorption: the primary reason is the existence of a large barrier to dissociation which increases as coverage decreases. We explain this coverage dependence through the involvement of substrate deformation in the adsorption geometry and energetics, and the diminishing ability of the adsorbates to produce this deformation as coverage drops. The secondary reason water remains molecular at low temperature is that it is not mobile and therefore cannot migrate to oxygen vacancies *or* to other molecules. Vacancies are well-known active sites for dissociation, but we have shown that neighboring molecules, through their H bonding, lower the dissociation barrier. We have also shown that photoelectron spectroscopy probably cannot distinguish between dissociated species on the perfect surface and those at oxygen vacancies.

The one unresolved question is: why does STM not see dissociated species on the perfect surface? If they are present, their contribution to the image must be understood, and we note that no dissociation geometries such as, e.g., Fig. 1(a) were used to generate the simulated images in Ref. 4. However, it is more likely that at temperatures sufficient to overcome the dissociation barrier, water is mobile enough for most adsorbates to find defect sites. There is also the question of how the substantial bias required, around 1.3 eV, affects the adsorbates. Our calculations show that at the level of the GGA within DFT, dissociated H_2O is the most stable state on the perfect surface, and therefore it seems worthwhile pursuing these points. Other methods of sample treatment—e.g., photoinduced dissociation at low temperature—may be helpful.

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offer an extended consideration of their work elsewhere (Ref. 48).

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