

## Molecular Chemisorption as the Theoretically Preferred Pathway for Water Adsorption on Ideal Rutile $\text{TiO}_2(110)$

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By taking careful account of slab thickness and adsorbate orientation effects we present, for the first time, periodic density functional calculations predicting the preference of water to adsorb in a molecular state on the ideal rutile  $\text{TiO}_2(110)$  surface at all coverages  $\leq 1$  monolayer (ML). Moreover, while this has been predicted previously for  $1/4$  ML coverage [R. Schaub *et al.*, Phys. Rev. Lett. **87**, 266104 (2001)], we show that the assertion made in that work, that dissociation is energetically *unfeasible* on the ideal surface, is incorrect. Our results thus resolve a long-standing discrepancy between theory and experiment and significantly improve the understanding of water chemistry on  $\text{TiO}_2$  surfaces.

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Despite extensive investigation, the chemical nature of water adsorbed on the ideal (110) surface of rutile  $\text{TiO}_2$  in ultrahigh vacuum (UHV) remains a highly controversial subject [1–3]. The issue is of particular importance as  $\text{TiO}_2(110)$  is considered *the* model system in metal-oxide surface science [1] and water is *the* prototypical probe for studying molecule-surface interactions [2]. Nevertheless, confusion persists regarding this system because (i) conclusions vary among numerous experimental reports, and (ii) significant discrepancies exist between experiment and theory. Regarding the first issue, experimentalists generally agree that at low temperatures in UHV molecular chemisorption dominates at all coverages [4–11]. Disagreements center around the extent of dissociation at various temperatures and whether dissociation is even possible on the ideal surface or only at defect sites [1–3]. As for the second issue, far from helping reconcile differences seen among experiments, theoretical studies have only added to the confusion as the vast majority have predicted complete or partial dissociation to be most favorable on the ideal surface at coverages  $\leq 1$  ML [12–17]. A handful of theoretical studies have been reported recently, however, predicting molecular adsorption to be preferred [10,18,19], apparently in agreement with experiment. Why these studies contradict those in Refs. [12–17] remains an open question, however, and it is thus unclear whether they truly represent a reconciliation between theory and experiment.

In this Letter, we address the controversy surrounding water adsorption on ideal  $\text{TiO}_2(110)$  and clear up the situation as it pertains to periodic density functional calculations, in particular. We show that these calculations predict molecular chemisorption to be most energetically favorable at coverages  $\leq 1$  ML despite a number of previous reports to the contrary [12–16]. We also refute a previous assertion that dissociation on the ideal surface is energetically unfeasible at low coverages [10]. We find that while molecular adsorption is indeed fa-

vored, dissociative adsorption does represent a stable thermodynamic state that might be accessible at elevated temperatures. Our results thus largely resolve the long-standing discrepancy between theory and experiment regarding the preferred mode for water adsorption on ideal  $\text{TiO}_2(110)$  and raise interesting new questions regarding adsorption at elevated temperatures in the process.

The Vienna *ab initio* Simulation Package (VASP) [20] was used for all density functional calculations reported in this work. Vanderbilt ultrasoft pseudopotentials [21] expanded in a plane-wave basis were employed (495 eV cutoff) and the PW91 [22] gradient corrected exchange-correlation functional was used.  $\text{TiO}_2(110)$  surfaces were modeled as periodic slabs and Brillouin zone sampling was on an  $8 \times 4$  Monkhorst-Pack [23]  $k$ -point mesh in the  $[001] \times [\bar{1}10]$  directions of the surface unit cell. No sampling was performed in the direction of the vacuum gap and surface plane sampling was reduced appropriately for larger surface supercells. Surface energies were calculated in the usual way as the difference in energy between the slab and the equivalent number of  $\text{TiO}_2$  units in the bulk, divided by the total surface area, and adsorption energies were calculated as the sum of the energies of the separated substrate and adsorbate less that of the substrate-adsorbate complex, divided by the total number of adsorbed molecules [24]. All water adsorption calculations were performed with identical adsorbates on each face of the slab and a vacuum gap of  $\sim 18$  Å was used (unless otherwise noted). In all cases, geometry optimizations were performed via conjugate-gradient minimization with an ionic relaxation convergence criterion of  $10^{-3}$  eV, and all atoms were allowed to fully relax in the three-dimensional space of the computational cell.

In Fig. 1 we show the three 1 ML adsorption configurations considered in this work. The fully molecular and dissociated structures shown in Figs. 1(a) and 1(b), respectively, have been considered previously by a number of authors [12,15–17], and the “mixed” structure shown in Fig. 1(c) is the same as that first reported by Lindan

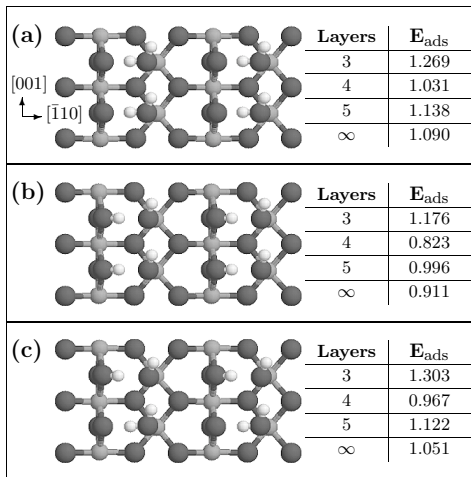


FIG. 1. Plan view of the three 1 ML adsorption modes: (a) molecular, (b) dissociative, (c) “mixed.” Ti atoms are shown in gray, O in black, and H in white. Four unit cells are shown for clarity. Adsorption energies are in eV/H<sub>2</sub>O and infinite-slab values are estimated using the “25% rule.”

*et al.* [15]. Also included in Fig. 1 are adsorption energies calculated for slabs of three to five layers [25] as well as infinite-slab estimates calculated using, what we term, the “25% rule.” The basis for the 25% rule is illustrated in Fig. 2 where we plot adsorption energies for both molecular and dissociative adsorption at ML coverage [Figs. 1(a) and 1(b), respectively], along with bare surface energies, for slabs of three to nine layers [26]. In each case we see that the converged energy values (estimated as the averages of the eight- and nine-layer values) lie  $\sim 25\%$  of the way between the three- and four-layer values (hence the 25% rule). The fact that this trend is observed for both bare surfaces and those with a full ML of coverage leads us to assume, therefore, that the rule holds for all sub-ML coverages as well. The 25% rule in itself thus represents an important result of this work. It demonstrates that the minimum computational effort necessary to obtain reliable estimates of the best possible theoretical values (i.e., those for infinitely thick slabs) at coverages  $\leq 1$  ML amounts to one three-layer calculation and one four-layer (assuming convergence is achieved with respect to basis set,  $k$  points, etc.). In situations requiring large surface supercells, such as in the study of low coverage water adsorption, this rule may thus prove invaluable in making a thorough investigation computationally feasible.

Returning to Fig. 1, we see that on the three-layer slab mixed adsorption is most energetically favorable. This result agrees with first-principles molecular dynamics (FPMD) simulations of Lindan and co-workers [15,16] who observed this mode for several runs on three-layer slabs. We also see, however, that increasing to a four-layer slab has an interesting, and unexpected, effect. The adsorption energies for all configurations decrease with the increase in slab thickness (as expected) but dissociated water molecules cause larger decreases than do molecu-

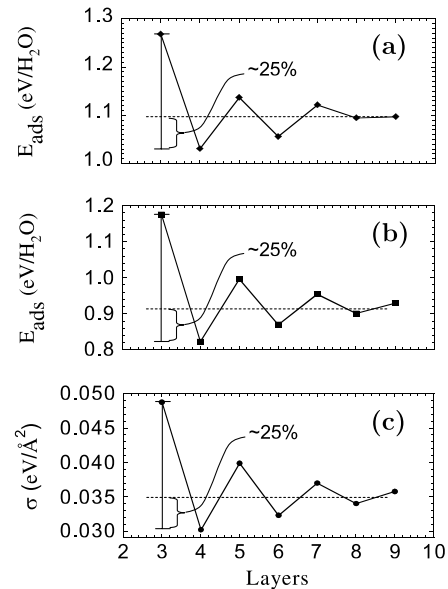


FIG. 2. Illustration of the 25% rule for (a) ML molecular adsorption [Fig. 1(a)], (b) ML dissociative adsorption [Fig. 1(b)], and (c) the bare surface energy. In all cases the seven-, eight-, and nine-layer values were calculated with  $\sim 9$  Å of vacuum, still sufficient to avoid interactions through the gap [17,27].

larly bound waters. The effect is such, in fact, that molecular adsorption overtakes mixed as the preferred mode on the four-layer slab. Moreover, this ordering is maintained on the five-layer slab and upon extrapolation to infinity using the 25% rule. These results demonstrate, therefore, that molecular chemisorption is the theoretically preferred adsorption pathway at ML coverage and may explain why previous FPMD studies [15,16] failed to reach the same conclusion [28]. Note also, however, that the difference in energy between molecular and mixed is small, suggesting that partial dissociation may be possible at elevated temperatures (as was suggested in Ref. [15] as well, in fact).

In Fig. 3 we show the three  $1/2$  ML adsorption configurations considered. Included are a molecular and two types of dissociative adsorption, which we term “inline” and “staggered,” respectively. We see first that on the three-layer slab dissociation is energetically favored and that the two dissociative modes are nearly degenerate in energy. The former result again agrees with FPMD simulations of Lindan and co-workers [14,16] while the latter coincides with first-principles calculations of Vogtenhuber *et al.* [29]. Increasing to a four-layer slab again has a dramatic effect on the relative energetics, however. The adsorption energies for the dissociative structures decrease by significantly more than that for the molecular and, as such, molecular adsorption becomes most favorable. The degeneracy between the dissociative modes is broken as well, with inline becoming favored relative to staggered. Moreover, the ordering is again maintained on the five-layer slab and upon extrapolation to infinity. Thus, molecular chemisorption is seen to be

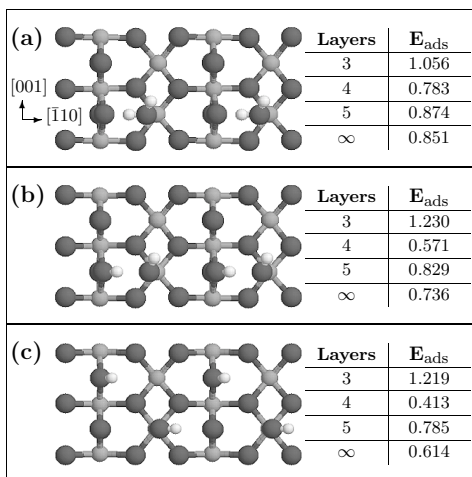


FIG. 3. Plan view of the three 1/2 ML adsorption modes: (a) molecular, (b) inline dissociative, (c) staggered dissociative. Illustration details are the same as in Fig. 1.

the preferred mode at 1/2 ML coverage, and again our results may explain why previous FPMD studies [14,16] failed to reach the same conclusion [30].

Finally, in Fig. 4 we show the three 1/4 ML configurations considered in this work. Again we consider a molecular, an inline dissociative, and a staggered dissociative mode, and again we see essentially the same behavior as previously: (i) On the three-layer slab dissociation is favored and both dissociative modes are similar in energy, (ii) increasing to a four-layer slab drastically affects the relative energetics with molecular adsorption becoming most favorable and inline becoming favored relative to staggered, and (iii) the result is maintained on the five-layer slab [31] and upon extrapolation to infinity. The important consequence of these results, therefore, is that they refute the contention made by Schaub *et al.* [10] that dissociation is energetically unfeasible on the ideal surface at this coverage (i.e., has a negative adsorption

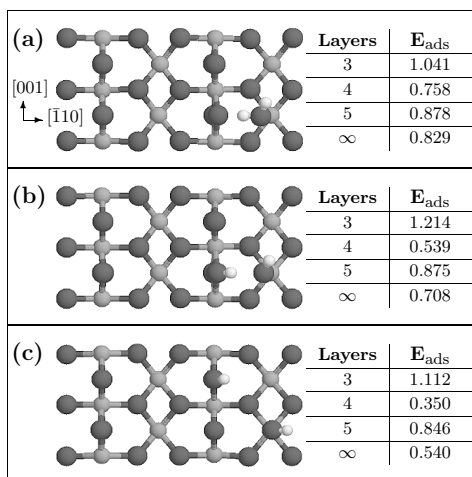


FIG. 4. Plan view of the three 1/4 ML adsorption modes: (a) molecular, (b) inline dissociative, (c) staggered dissociative. Illustration details are the same as in Fig. 1.

energy). The reason for the discrepancy between our results and theirs, however, is somewhat unclear. The technical details of their calculations are, in fact, quite similar to ours with the only major difference being that in [10] adsorbates were placed on only one face of the computational slab. We checked to see if this could account for the discrepancy and found that while the adsorption energies (on three-layer slabs) increase somewhat for each of the configurations [1.071, 1.428, and 1.371 for Figs. 4(a)–4(c), respectively] the relative energetics remain unchanged. The discrepancy, therefore, likely lies in the details of the adsorption geometries considered by Schaub *et al.*, of which, unfortunately, there are no detailed illustrations. Note, however, that the adsorption energies given in Fig. 4 are quite similar to those for the 1/2 ML modes in Fig. 3 when comparing between similar counterparts. Given that the only difference between the sets of modes is the absence of an adsorbate in the  $[\bar{1}10]$  direction for the 1/4 ML structures, this suggests that interactions between adsorbates in  $[\bar{1}10]$  are weak relative to those in  $[001]$ . This was suggested previously by Lindan *et al.* [15], in fact, and thus provides substantial support for our calculations. In other words, the calculation in  $[10]$  of a negative adsorption energy for dissociation at 1/4 ML coverage runs contrary to the well-documented results at 1/2 ML coverage [14–16,29] and the expected minimal effect of removing a neighboring water molecule in the  $[\bar{1}10]$  direction [15]. Our results, which coincide with the expected behavior, thus appear to warrant the confidence ascribed them.

In conclusion, via an extensive periodic density functional investigation of water adsorption on ideal rutile  $\text{TiO}_2(110)$  we have shown that molecular chemisorption represents the theoretically preferred adsorption pathway at all coverages  $\leq 1$  ML [32], in agreement with numerous low temperature UHV studies reported in the literature [4–11]. Furthermore, we have shown that at ML coverage a mixed adsorption state exists that is slightly higher in energy, and that at low coverage dissociative adsorption is thermodynamically stable, contrary to a previous assertion [10]. These results suggest, therefore, that although molecular chemisorption is most favorable on ideal  $\text{TiO}_2(110)$ , dissociation *might* be accessible at elevated temperatures. It has been argued previously, however, that desorption, in fact, occurs instead [7] and that dissociation occurs only at defect sites [6,9,10]. The issue remains, nonetheless, controversial. In particular, temperature programmed desorption (TPD) experiments [5,6,8] reveal a first-layer desorption feature whose peak position decreases with increasing initial coverage. A conclusive explanation for this behavior has yet to be offered and the fact that we show adsorption energies increasing with coverage suggests that the desorption kinetics are more complex than previously thought [33]. Brinkley *et al.* [8] argued, however, that the TPD results indicate desorption from a heterogeneous surface containing numerous types of binding sites, thus supporting

the idea that surface defects are crucial for dissociation. Although an intriguing premise, we offer a somewhat different explanation: The heterogeneity need not necessarily be associated with the surface but may exist within the adsorbed layer itself (as was suggested in Ref. [5], in fact). In other words, as the temperature is increased in TPD dissociation may occur, resulting in an inhomogeneous adlayer composed of both molecular and dissociated water molecules (of various relative orientations [34]). Moreover, at low coverages the dissociated fragments may become free to migrate and separate. Desorption would then depend upon the rate at which these fragments recombine, and if diffusion is rate limiting desorption may occur at higher temperatures despite the fact that adsorbates are less strongly bound at low coverages. Of course, at this point we can only speculate as to this scenario, but perhaps this work will motivate further investigation into the subject.

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- [25] Slab thickness is defined as the number of O-Ti<sub>2</sub>O<sub>2</sub>-O layers comprising the computational slab.
- [26] The physical basis for the oscillatory convergence behavior has been discussed in detail elsewhere for both bare [27] and water adsorbed [17] TiO<sub>2</sub>(110) surfaces.
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- [28] Although the FPMD simulations in [15,16] were performed on three-layer slabs, the adsorption energies reported were for five- and seven-layer slabs, respectively. In [15] these calculations showed mixed adsorption to be most favorable at ML coverage while in [16] a stable molecular state could not be identified via FPMD. Slab thickness effects may thus explain the result in [16] but not those in [15]. The use of a different basis set and fewer *k* points in [15] may, however. Nonetheless, the observations of mixed adsorption in FPMD in [15,16] are consistent with our three-layer results.
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- [30] Again, slab thickness effects cannot explain why inline dissociative was favored at 1/2 ML coverage on a seven-layer slab in [16]. The FPMD observations in [14,16] are, nonetheless, consistent with our three-layer results.
- [31] Although here the difference between molecular and inline dissociative is within the error bars of the calculation. Nevertheless, the clear preference for molecular adsorption is apparent via the “25% rule.”
- [32] In [16], and confirmed by our own unpublished results, it was shown that adsorbate asymmetries in the [001] direction minimally affect the adsorption energetics. That interactions in [110] also appear to be minimal suggests, therefore, that asymmetry effects are unlikely to alter the relative energetics between modes. The results presented here should thus be generally representative of all possible ML/sub-ML adsorption states.
- [33] Lindan *et al.* [15] also reported larger adsorption energies at higher coverages, but in comparing to the TPD results they incorrectly associated the larger values with the higher temperature (hence, lower coverage) part of the feature, and vice versa.
- [34] Although adsorbate asymmetries are unlikely to affect the relative energetics [32], they may contribute to the broadness of the first-layer TPD feature [5,6,8].