

Reply to “Comment on ‘Structure and dynamics of liquid water on rutile TiO₂(110)’”

Li-Min Liu, C. Zhang, G. Thornton, and A. Michaelides

London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, United Kingdom

(Received 5 December 2011; published 5 April 2012)

The water-TiO₂(110) interface is as important as it is controversial. In our recent density functional theory (DFT) study [Liu *et al.*, *Phys. Rev. B* **82**, 161415 (2010)], we showed (with several different exchange-correlation functionals) that water does not dissociate on the perfect TiO₂(110) surface when care is taken to avoid artifacts resulting from the simulation cell used. Here, we report additional DFT-based molecular dynamics results that further support this view. We also briefly discuss some of the challenges involved in obtaining molecular-level understanding of the water-TiO₂(110) interface. These are challenges that we, Wesolowski and co-workers, and many others have faced, challenges which have served to make this such an interesting and controversial system.

DOI: [10.1103/PhysRevB.85.167402](https://doi.org/10.1103/PhysRevB.85.167402)

PACS number(s): 68.43.Bc, 68.47.Gh, 82.30.Rs, 82.65.+r

It is often stated that under ambient conditions, most surfaces are covered in a thin film of water and, as such, the properties of wet surfaces are of the utmost importance to many technological processes as well as to many aspects of daily life. Of all the many and varied water-solid interfaces, the water-TiO₂ interface has probably been examined by more groups from more different fields than any other. Partly this is because wet titanium dioxide (TiO₂) surfaces are directly relevant to an increasingly long list of technological and scientific areas, such as photocatalysis and energy production. However, partly this is because the water-TiO₂ interface is highly controversial, particularly when it comes to molecular-level understanding of the structure and dynamics of water in the immediate vicinity of the TiO₂ surface.

Liu *et al.*¹ report our results from an extensive set of first-principles simulations for water overlayers and liquid water films on pristine rutile TiO₂(110). In the comment by Wesolowski *et al.*,² they review their work on this and another system and question certain details of the calculations we performed. Here, we address the issues raised by Wesolowski *et al.*, which directly relate to our paper.

One of the key issues about the structure of interfacial water on TiO₂(110) is whether the molecules dissociate at the surface. Experimentalists and theorists have long debated this matter, with theorists reaching different conclusions depending on the particular electronic structure theory (mainly flavor of density functional) or surface model used (see, e.g., Refs. 1 and 3–15). As our first venture with *ab initio* methods into the water-TiO₂(110) system, we began by meticulously addressing the issue of water dissociation. We showed in Liu *et al.*¹ through a series of painstaking calculations that, for a range of water coverages and for frozen and liquid overlayers, if the simulations are carefully converged, all exchange-correlation functionals considered produce the same result. Water does not dissociate on the perfect TiO₂ surface according to state-of-the-art density functional theory (DFT) calculations (see Fig. 1 in Ref. 1). Our analysis also included results from the first hybrid functional calculations for periodic water overlayers on TiO₂, simulations, which because of their computational cost have only recently become feasible. Wesolowski *et al.* repeated some of our total energy geometry optimizations after we supplied them with our coordinates and they reproduced our results. One of the key results of the geometry optimizations is that irrespective of the exchange-correlation functional

used, nonconverged results are obtained if water adsorption is examined on three- and five-layer TiO₂ slab models. Therefore, it is unfortunate that Wesolowski *et al.* did not perform similar convergence tests at the outset of their studies and have by now based so much of their DFT work, subsequent classical molecular dynamics (MD) studies, and rationalization of experimental results on nonconverged slab models.

Very long *ab initio* MD (AIMD) simulations are not possible since unlike the simple classical MD simulations performed by Wesolowski *et al.*, they are computationally expensive. The simulations reported in Liu *et al.* were limited to 25 ps. Wesolowski and co-workers, quite reasonably, question whether this is long enough to observe dissociation. However, we are confident that our AIMD simulations have been run for long enough to provide a reliable answer to the question of water dissociation and report additional evidence for this in Fig. 1. This figure shows the results of three AIMD simulations performed with different TiO₂ slab models and different initial conditions at 1 ML. As shown in Fig. 1, no water dissociation is observed during the course of the 25-ps simulation for the water monolayer on a four-layer slab. When a simulation is started with half the molecules initially dissociated (four out of the eight molecules in the simulation cell) on the four-layer slab, the water molecules quickly *recombine* until at about 20 ps no dissociated water molecules remain [Fig. 1(b)]. In contrast, starting a simulation on a three-layer slab with an overlayer of intact water molecules quickly leads to an overlayer in which most of the water molecules are dissociated [Fig. 1(c)]. From these simulations, it is clear that the level of water dissociation is not sensitive to the initial state used in the AIMD simulations.

Establishing answers from first-principles theory for the defect-free surface was the main aim of Liu *et al.*, and we very clearly pointed this out. It is impossible to gauge the defect density in the diffraction experiments of Wesolowski and co-workers⁷ with any accuracy. They do not prepare their samples in ultrahigh vacuum (UHV) and they are not reduced under UHV in order to achieve atomic-level characterization. The only “characterization” performed is with x-ray diffraction, which is not sensitive to low levels of disordered defects in the form of say O vacancies.⁷ It is well known that water dissociation takes place at defect sites on TiO₂. For example, ambient pressure photoemission work shows dissociation at defects, which then nucleates

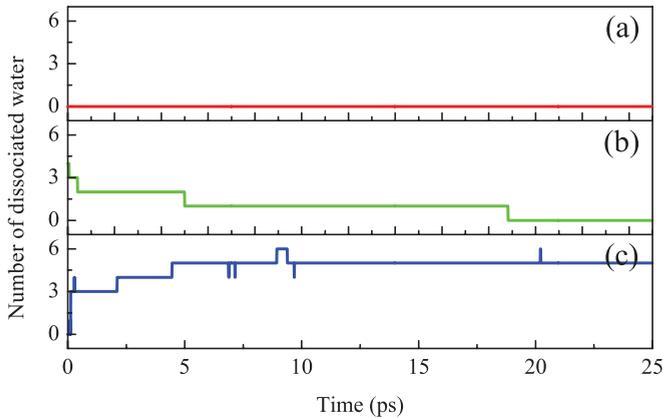


FIG. 1. (Color online) Number of dissociated water molecules at the TiO_2 surface as a function of simulation time for three *ab initio* molecular dynamics simulations at a coverage of 1 ML. (a) An overlayer of intact water molecules on the four-layer TiO_2 slab. No dissociation takes place during the simulation. (b) An overlayer on a four-layer slab with four out of the eight water molecules initially dissociated. As the simulation progresses, water molecules recombine until at about 20 ps no dissociated water molecules remain (i.e., all adsorbed OH and H groups recombine). (c) An overlayer of initially intact water molecules on a three-layer slab. Unlike on the four-layer slab, dissociation of water molecules is quickly observed. Results are for the PBE functional at 360 K with the computational setup the same as that reported in Ref. 1.

molecular water growth.⁵ On this basis, it seems very likely that any apparent discrepancy between our DFT results and the diffraction work of Wesolowski and co-workers is associated with a small concentration of vacancies or other surface defects in the experiment.

Even though it is likely that there is some level of water dissociation in the x-ray diffraction experiments of Wesolowski and co-workers, it is important to remember that no direct evidence for water dissociation is actually obtained by Zhang *et al.*,⁷ which is why we say “apparent discrepancy.” Rather, water dissociation is inferred and the estimate of 30% water dissociation is obtained from a somewhat questionable and opaque procedure. Specifically, it is arrived at using a model of an ordered O atom overlayer from which a single best-fit Ti-O distance is extracted. It is then speculated that this is an average distance for a mixture of Ti-OH and Ti-H₂O bonds by making reference to their own DFT calculations. By comparing the extracted distance to the best-fit distance obtained from another system (1 molal RbCl + RbOH solution at pH 12) and assuming that the bonding at the surface is unaffected by changes in solution conditions and Rb adsorption at the surface, an estimate of $30 \pm 15\%$ dissociation is eventually arrived at. Clearly, this can be considered a crude estimate at best and, while it is very likely that the defects inevitably present on the experimental crystal surface induce dissociation, it is somewhat irrational to conclude that this estimate represents evidence of a problem with our AIMD simulations. Before moving on, it is worth pointing out that using planar-averaged density profiles is not a particularly straightforward criterion for distinguishing molecular from dissociated water in this particular system. While the Ti-H₂O and Ti-OH bond lengths differ significantly (e.g., 2.25 and

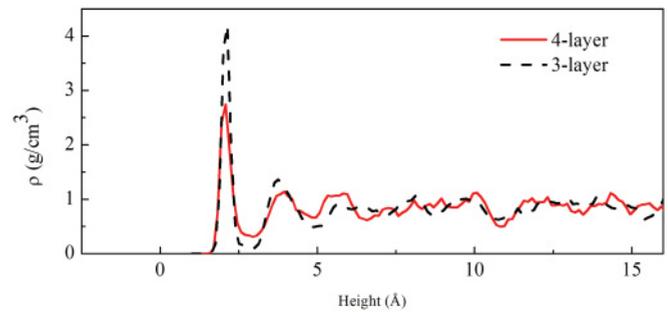


FIG. 2. (Color online) Mass density versus the height above the surface obtained from *ab initio* molecular dynamics simulations for water films on four-layer and three-layer TiO_2 slabs. On the four-layer slab, all the water molecules remain intact, whereas on the three-layer slab, water dissociation takes place. Despite the different chemical nature of the first contact layer, the first peak in the density profile remains at a similar distance above the surface in each simulation. The average position of the TiO_2 surface layer is defined as zero. Results are for the PBE functional at 360 K with the computational setup the same as that reported in Ref. 1.

2.05 Å, respectively, from our calculations), the average height of the first liquid layer above the surface is very similar regardless of whether water is dissociated or not, as shown in Fig. 2. Specifically, the first maximum in the planar-average density profile is at 2.1 Å for a liquid water film containing only intact water molecules and also at 2.1 Å for a liquid water film where there is about 60% dissociation at the interface. The similar height of the first layer above the surface in each system results from relaxations of Ti_{5c} atoms at the surface, relaxations that were not accounted for in the classical MD simulations of Wesolowski *et al.*

Wesolowski *et al.* argue that the extent of layering in our AIMD simulations is inconsistent with what they obtain from their x-ray diffraction data and classical MD simulations. Looking at this issue with some perspective, we think that the qualitative agreement between our AIMD simulations and experiment is as good as one could hope to obtain in such a complex system. This is particularly true given the issues noted above about dissociation and the difficulty in fitting x-ray data above the “first” layer. The experimental data are interpreted as suggesting three layers at the interface, and in our simulations we have two clear layers and a weak third layer. Both experiment and theory agree over the location of the water molecules in the first two layers, above Ti and bridging oxygen sites in layers 1 and 2, respectively. Likewise, the qualitative agreement between our *ab initio* MD simulations and Wesolowski *et al.*’s force-field simulations is about as good as one would expect (cf. Fig. 2 in Ref. 1 and Fig. 4 in Ref. 16). Given the simplicity of the force-field description used by Wesolowski *et al.* (rigid nonpolarizable SPC/E water, a fixed TiO_2 slab, and a pair-wise Lennard-Jones potential for the interaction with the surface) and the complexity of the water- TiO_2 interaction, it would be unlikely if anything better than qualitative agreement was obtained between the two sets of simulations. The higher degree of layering observed in Wesolowski *et al.*’s simulations is likely due to their choice of a three-layer TiO_2 model during the initial DFT parametrization of the water- TiO_2 interaction model. As shown in Table I,

TABLE I. Adsorption energies E_{ads} (eV/water) at 0.5 and 1 ML for three-, five-, and nine-layer slabs with different methods. $E_{\text{ads}} = E_{\text{TiO}_2(110)} + E_{\text{water}} - E_{\text{water/TiO}_2(110)}$, where $E_{\text{TiO}_2(110)}$, E_{water} , and $E_{\text{water/TiO}_2(110)}$ are the total energies of the clean $\text{TiO}_2(110)$ surface, the appropriate number of isolated gas-phase water molecules, and the whole adsorption system, respectively. In each case, the most stable state is indicated in bold. All water molecules are intact in the ‘‘INTACT’’ column. In the ‘‘PDIS’’ column, half the water molecules are dissociated, and in the ‘‘DIS’’ column, all water molecules are dissociated. Calculations were performed with VASP with the computational setup reported in Ref. 1.

Layers	Method	0.5 ML		1 ML			Ref.
		INTACT	DIS	INTACT	PDIS	DIS	
3	PBE	0.75	0.96	0.90	0.97	0.94	
	HSE06	0.94	1.19	1.01	1.10	1.08	
	PW91	0.93	1.15	1.08		0.98	17
	Force field	1.25		1.14			17
5	PBE	0.74	0.75	0.81	0.80	0.73	
	HSE06	0.89	0.89	0.90	0.90	0.76	
	PW91			0.94		0.80	17
	Force field			1.12			17
9	PBE	0.68	0.57	0.79	0.73	0.61	
	HSE06	0.84	0.74	0.91	0.85	0.75	

the force-field adsorption energies of molecular water on a three-layer slab¹⁷ can be overestimated by as much as 0.2–0.4 eV relative to the results obtained with DFT (either with generalized gradient approximation functionals or hybrid functionals). Such an overestimate of the adsorption would undoubtedly lead to artificially enhanced layering at the interface.

Enhanced layering at the surface because of an overestimated surface interaction is also very likely to reduce the water diffusion rate at the surface. It is not surprising therefore that Wesolowski *et al.* observe more sluggish water diffusion than we do in their classical MD simulations. Wesolowski *et al.* dispute our conclusion that the value obtained for the diffusion coefficient of the water molecules in the second layer above the surface (0.07 Å²/ps) is characteristic of Perdew-Burke-Ernzerhof (PBE) bulk water at our target temperature of 360 K. This again is a reasonable concern since in choosing an accurate *ab initio* description of the electronic structure, we must compromise on system size and total run time (our system comprised 91 water molecules and 64 TiO₂ formula units). To test the particular issue, we performed a bulk water PBE simulation in a box containing 64 molecules at 360 K. The diffusion coefficient obtained is 0.05 Å²/ps. Thus, we are confident in the veracity of our conclusions, although it goes without saying that the statistical error bar on all AIMD simulations will be larger than what one can obtain with cheaper empirical potentials. Of course, the absolute value of the diffusion coefficient obtained from DFT-PBE is far below the experimental value. This is one of many well-known problems with widely used exchange-correlation functionals such as PBE and the reason we performed AIMD simulations at 360 K. It is encouraging that much improved properties for the structure and dynamics of liquid water can now be obtained

with van der Waals density functionals such as optB88-vdW (Refs. 18 and 19) and it would be interesting in the future to apply these functionals to liquid water on TiO₂.

More generally, controversies abound in studies of water-solid interfaces because it is incredibly difficult to characterize the structure and dynamics of liquid adlayers under ambient conditions. There is simply no single technique that offers the detailed structural and temporal resolution we all desire. Experiment finds it challenging to obtain atomic-level understanding of interface structures outside UHV conditions and theory struggles because of the need for a very accurate description of the intermolecular forces involved, the need to run long simulations, and large unit cells. In an area such as this, it is all too easy to confuse experimental results with inferences made from experimental data. Likewise, it is tempting to take satisfaction in a simulation result that appears to agree with experiment. However, if real progress is to be made, one should move beyond simulations that are ‘‘right for the wrong reasons’’² toward those which are right for the right reason. Of course, there remains a long way to go until theory truly reaches this point, e.g., the first application of quantum Monte Carlo to water adsorption has just appeared but was limited to adsorption of a single water monomer.²⁰ However, for the time being, it can not hurt to, at least, make an attempt to obtain converged results with current state-of-the-art methods.

This work was supported by the European Research Council. Computational resources from the London Centre for Nanotechnology, UCL Research Computing, and the UK’s national high performance computing service HECToR (for which access was partly obtained via the UK’s Material Chemistry Consortium, EP/F067496) are warmly acknowledged.

¹L. M. Liu, C. J. Zhang, G. Thornton, and A. Michaelides, *Phys. Rev. B* **82**, 161415 (2010), and references therein.

²D. Wesolowski *et al.*, *Phys. Rev. B* **85**, 167401 (2012), and references therein.

- ³C. H. Sun, L. M. Liu, A. Selloni, G. Q. Lu, and S. C. Smith, *J. Mater. Chem.* **20**, 10319 (2010).
- ⁴M. A. Henderson, *Surf. Sci.* **355**, 151 (1996).
- ⁵G. Ketteler, S. Yamamoto, H. Bluhm, K. Andersson, D. E. Starr, D. F. Ogletree, H. Ogasawara, A. Nilsson, and M. Salmeron, *J. Phys. Chem. C* **111**, 8278 (2007).
- ⁶S. Wendt, R. Schaub, J. Matthiesen, E. K. Vestergaard, E. Wahlstrom, M. D. Rasmussen, P. Thostrup, L. M. Molina, E. Laegsgaard, I. Stensgaard, B. Hammer, and F. Besenbacher, *Surf. Sci.* **598**, 226 (2005).
- ⁷Z. Zhang, P. Fenter, N. C. Sturchio, M. J. Bedzyk, M. L. Machesky, and D. J. Wesolowski, *Surf. Sci.* **601**, 1129 (2007).
- ⁸L. A. Harris and A. A. Quong, *Phys. Rev. Lett.* **93**, 086105 (2004).
- ⁹P. J. D. Lindan, N. M. Harrison, and M. J. Gillan, *Phys. Rev. Lett.* **80**, 762 (1998).
- ¹⁰C. Zhang and P. J. D. Lindan, *J. Chem. Phys.* **119**, 9183 (2003).
- ¹¹W. H. Zhang, J. L. Yang, Y. Luo, S. Monti, and V. Carravetta, *J. Chem. Phys.* **129**, 064703 (2008).
- ¹²B. Hammer, S. Wendt, and F. Besenbacher, *Top. Catal.* **53**, 423 (2010).
- ¹³K. Jug, N. N. Nair, and T. Bredow, *Surf. Sci.* **590**, 9 (2005).
- ¹⁴W. Langel, *Surf. Sci.* **496**, 141 (2002).
- ¹⁵Z. Dohnalek, I. Lyubinetsky, and R. Rousseau, *Prog. Surf. Sci.* **85**, 161 (2010).
- ¹⁶M. Predota, A. V. Bandura, P. T. Cummings, J. D. Kubicki, D. J. Wesolowski, A. A. Chialvo, and M. L. Machesky, *J. Phys. Chem. B* **108**, 12049 (2004).
- ¹⁷A. V. Bandura and J. D. Kubicki, *J. Phys. Chem. B* **107**, 11072 (2003).
- ¹⁸J. Klimes, D. R. Bowler, and A. Michaelides, *J. Phys.: Condens. Matter* **22**, 022201 (2010).
- ¹⁹C. Zhang, J. Wu, G. Galli, and F. Gygi, *J. Chem. Theor. Comput.* **7**, 3054 (2011).
- ²⁰J. Ma, A. Michaelides, D. Alfè, L. Schimka, G. Kresse, and E. G. Wang, *Phys. Rev. B* **84**, 003402 (2011).