First-principles molecular dynamics simulation of water dissociation on TiO$_2$ (110)

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Abstract
We have performed first-principles molecular dynamics calculations of water adsorption on TiO$_2$ (110). We find that dissociative adsorption occurs at the fivefold-coordinated Ti site resulting in the formation of two types of hydroxyl group. The vibrational spectra calculated from this hydroxylated surface show that a clear stretch frequency is present for only one of these groups, with vibrations from the other hydroxyl broadened due to hydrogen bonding between the two hydroxyl groups.
1 Introduction

The observation [1] of photoelectrolysis of water by TiO$_2$ has stimulated much effort to understand water adsorption on its surfaces. Further motivation has come from the widespread application of TiO$_2$ powder as a white pigment: surface properties are strongly influenced by water adsorption which occurs, for example, when the powder is exposed to air. However, there is still uncertainty as to the state (molecular or dissociative) in which adsorption occurs on the defect-free surface [2]. In this paper we report first-principles molecular dynamics (MD) studies of water on the (110) surface of TiO$_2$, which we performed with two main objectives in mind. The first was to clarify theoretical predictions concerning dissociative adsorption on the perfect surface. MD provides a natural way to explore molecular configurations on the surface, and to find the most favourable adsorption mechanism. Our second aim was to use the dynamical information from the calculations to shed light on recent vibrational spectroscopy [3]. In particular, the vibrational signatures of adsorbed species need to be determined.

Experimental techniques including temperature-programmed desorption (TPD), ultraviolet and x-ray photoemission spectroscopies (UPS and XPS), high-resolution electron-energy loss spectroscopy (HREELS) and work function measurements have been applied to this system. Studies of microcrystalline powders [4] indicate that water dissociation occurs on TiO$_2$ surfaces and that the (110) surface is the most active. However, single-crystal UHV studies, which are of most relevance to the present work, are at some variance. Kurtz et al [5] used UPS to study water adsorption on the nearly-perfect and oxygen-defective TiO$_2$(110) surface. They found that dissociative adsorption occurs on the perfect surface at 300 K, with a saturation coverage of much less than a monolayer$^1$ (ML) and with little variation when surface defects are induced. At 160 K molecular adsorption was observed, which saturated at one ML; subsequent heating produced dissociation of some of the adsorbed molecules. Hugenschmidt et al [6] used XPS and work function measurements to assist interpretation of their TPD spectra. After exposure at 100 K, peaks at 160 K and 170 K were attributed to multilayer water and water hydrogen-bonded to bridging oxygens respectively, and a peak at 275 K to molecular adsorption at fivefold coordinated Ti sites. Using the UPS results of Kurtz et al, these authors attributed a high-temperature tail extending

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$^1$We define a monolayer as one water molecule per surface unit cell.
to 375 K to dissociatively adsorbed water; the coverage was estimated at 0.25 ML. A small TPD peak at 500 K was associated with surface hydroxyl groups bound to thermally-generated oxygen defects at 1% concentration. In addition to TPD, Henderson [3] has used HREELS to investigate the vibrational spectra of adsorbed water on TiO$_2$ (110). The TPD features he found were very similar to those of Hugenschmidt et al, and were interpreted in a similar way. However, Henderson argues that at 130 K, water dissociation occurs only at rather low coverages (~ 0.1 ML) and suggests that this occurs at defect sites. Vibrational spectra were used to support the view that the majority of first-layer adsorption was molecular, in particular, a feature at 1625 cm$^{-1}$ identified as the water bond-bending mode, and features around 3400 cm$^{-1}$ which were assigned to the O-H stretch modes of the molecule. Dissociative adsorption was linked with an O-H stretch feature at 3690 cm$^{-1}$ and it was noted that two distinct O-H frequencies expected from the two types of hydroxyl formed by dissociated water could not be observed. Infrared spectroscopy of TiO$_2$ powders does evidence at least two types of adsorbed O-H [4].

There are some theoretical treatments of water adsorption on TiO$_2$ surfaces in the literature. Semiempirical studies of single-molecule adsorption and hydroxylation [7, 8, 9] have been performed, but it is not clear that these can reliably predict the energetics involved. Hartree-Fock calculations [10] indicate that water adsorbs dissociatively on TiO$_2$ surfaces. All of these studies suffer from the limitation that the surface species were confined to highly symmetric configurations.

Since the work of Car and Parrinello [11], first-principles plane-wave pseudopotential techniques based on density-functional theory (DFT) have become quite standard and widely used on metals, insulators and semiconductors. Many static calculations have been reported which demonstrate the excellent agreement with experiment for structures and energetics which the method can give [13, 14]. There has been much DFT work on oxides [15], including several studies of TiO$_2$ bulk [16] and surface [17, 18] properties and surface reconstructions [19]. Very recently, static calculations of water adsorption on the (110) surfaces of TiO$_2$ and SnO$_2$ have been made by Goniakowski and Gillan [20]. These showed that dissociative adsorption was favourable for both materials, and the authors were unable to find any stable molecular adsorption geometry.

Trajectories from molecular dynamics (MD) provide a way to explore phase space, and a means to calculate equilibrium properties as averages over the tra-
jectory [21]. First principles MD based upon reliable and accurate forces may be used to study changes in chemical bonding which are inaccessible to simulations based on empirical potentials. However, such studies are much more demanding than static calculations, and there are correspondingly fewer examples in the literature. The first application to molecular processes at surfaces dealt with chlorine dissociation on silicon [22] and of water adsorption on defective MgO (100) [23].

In section 2 we explain the techniques employed, and the special considerations needed for MD. In section 3 we present and discuss our results. Whilst the majority are for TiO$_2$, we have also performed calculations for the closely-related material SnO$_2$, and we comment on the results of these calculations here. Finally, we present our conclusions in section 4.

2 Techniques

We have used a variant of the 	exttt{cetep} code [12], the parallel version of 	exttt{castep} [13], running on the 512-node CRAY T3D at the Edinburgh Parallel Computer Centre, to perform our calculations. The generalised-gradient approximation (GGA, [27, 28]) is used in preference to the local density approximation (LDA) as it provides a more accurate description of molecular dissociation energies and of hydrogen bonding [24, 25].

We have constructed norm-conserving pseudopotentials in the Kleinman-Bylander representation [29], optimised using the scheme of Lin et al [30], for titanium and oxygen [31]. A plane wave cutoff energy of 750 eV was found to converge the total energy of the 6-ion TiO$_2$ unit cell to 0.07 eV. The calculated lattice parameters (experimental values [32] in parenthesis) are 4.69 (4.594) and 2.99 (2.959) Å for $a$ and $c$ respectively, while the internal coordinate $u$ was 0.306 (0.305). The slight overestimation of the lattice parameters (2% for $a$) is typical for the GGA.

A 3D supercell is used to model the surface geometry (figure 1). The (110) surface normal is in the $z$-direction with (110) faces separated by a vacuum gap of $\sqrt{3}a$. The surface unit cell is doubled in the crystallographic [001] ($x$) direction creating a $2 \times 1$ cell containing 36 ions. The slab is 9 atomic layers thick, i.e. three O—Ti—O—O layers.

In order to minimise the computational cost the Brillouin zone sampling was restricted to the $\Gamma$-point and the hydrogen mass was set to 3 a.m.u. This
higher mass allows a longer time step to be used in the MD simulation without affecting configuration energies or equilibrium statistical averages such as vibrational mean-square displacements. The features in vibrational spectra will also be unaffected, but the hydrogen frequencies will be lower. This is taken into account when interpreting frequencies. The vibrational frequencies of a single water molecule have been computed within the harmonic approximation in order to validate this approach, and are shown in table 1. With a mass of 1 a.m.u excellent agreement with experiment is obtained. A mass of 3 a.m.u lowers the angle-bending frequency to 29 THz, still well clear of the TiO₂ lattice vibrations, and allows us to use a time-step of up to 2 fs in the MD. The bond length and bond angle of the water molecule were found to be 0.967 Å and 105°, again in excellent agreement with the experimental values of 0.957 Å and 104.5° [33].

After relaxation and equilibration of the ions in the slab at 500 K, a water molecule was placed on each surface in the simulation box in a variety of initial configurations which are discussed in detail in the following section. Initial, random velocities corresponding to a temperature of 500 K were assigned for all the ions; the water molecules were not given an overall velocity directed towards the surface to hasten adsorption.

3 Results and discussion

3.1 Adsorption simulations

Kurtz et al [5] have proposed a model for dissociation in which initially, molecular adsorption occurs at the fivefold-coordinated Ti site (marked in figure 1). We have performed several simulations in which water molecules were positioned with their oxygen atoms 3 Å above this site: figure 2a shows a typical starting configuration, with the molecule in the (110) plane. This corresponds to coverage of 0.5 ML. The behaviour observed in the dynamical simulations was as follows: in the early stages the molecule was drawn down to the surface rapidly, and its favourable orientation was in the (001) plane, with the oxygen atom pointing towards the the surface (figure 2b); when the oxygen atom is within about 2.7 Å of a bridging oxygen ion, there is strong interaction between a hydrogen and the bridging oxygen (figure 2c); this hydrogen atom is captured by the bridging oxygen, and the hydroxyl remnant of the water molecule adsorbs above the fivefold Ti site (figure 2d). It was noticable that while the hydroxyl
remnant is rather free with respect to its orientation, the hydrogen ion bonded to the bridging oxygen prefers to point towards the “water” oxygen from whence it came. This pattern of dissociative adsorption was seen for several initial orientations of the water molecules, and is apparently insensitive to the hydrogen positions as long as each molecule is near to a fivefold Ti site. The dissociation described took about 0.4 ps, and during a further 0.8 ps simulation time there was no change in the average hydroxyl positions. Almost identical behaviour was observed in similar simulations of water adsorption on SnO$_2$ (110), which has the same rutile crystal structure as TiO$_2$.

After relaxation of the ions at the end of these simulations, the geometry confirms that the water molecule is dissociated. For convenience we will use the term “terminal hydroxyl” to describe the O-H fragments which originate from the water molecule, and “bridging hydroxyl” to indicate the O-H group formed by a bridging oxygen and a hydrogen ion. The terminal hydroxyl bond length of 0.97 Å is little changed from that in the water molecule while in the bridging hydroxyls it is somewhat longer - 1.00 Å. The distance between the oxygen of the terminal hydroxyl and the hydrogen of the bridging hydroxyl is about 1.8 Å, and the H-O-H angle is about 120°. The angle was hard to determine accurately because the energy is weakly dependent on terminal hydroxyl orientation. The oxygen of the terminal hydroxyl is 2.8 Å from the bridging oxygen, and 1.90 Å above the fivefold titanium; the latter is displaced out of the surface by about 0.5 Å. In fact, the oxygen of the terminal hydroxyl basically completes the octahedral coordination of the titanium ion, occupying roughly the same position with respect to the titanium as would be taken by oxygen in the bulk crystal. The energy of adsorption obtained from our Γ-point calculations is 1.35 eV per H$_2$O at half-ML coverage. Our calculated geometry is in good agreement with static, multiple-κ-point DFT-GGA calculations [20]. The static calculations yielded an adsorption energy of 1.08 eV at monolayer coverage, and also indicated that at lower coverages the adsorption energy should increase.

We have performed similar calculations starting with water molecules over the 6-fold coordinated Ti site. Here, we chose orientations in which the hydrogen ions were closest to the bridging oxygens, but we could not find a position in which the molecule was attracted to the surface. This is in contrast to the 5-fold site simulations. Indeed, the repulsion made it necessary to do the calculations with only one water molecule in the simulation box, since the increased molecule-surface separation required brought the two molecules into close proximity in
the vacuum region. Dynamics simulations did not result in either physisorption or dissociation at the 6-fold site. Instead, the water molecule drifted away from the site and would presumably dissociate at the 5-fold site given sufficient simulation time.

3.2 Vibrational analysis of the simulations

We have used MD to calculate the vibrational power spectra of the hydrogen atoms from the temporal Fourier transform of their velocity autocorrelation function (vacf). In this way we can examine temperature effects, such as possible anharmonic shifts, not accessible in a harmonic analysis. We recall that, since we are using a hydrogen mass of 3 a.m.u., our calculated frequencies are lower than those that would be obtained with normal \( \text{H}_2\text{O} \), and must be corrected for purposes of comparison. The harmonic analysis (table 1) indicates a correction factor of 1.61-1.67 for the water molecule stretch frequencies, which we will use here. The vacf’s were calculated up to 1.05 ps, with time origins at every time-step, giving a resolution of \( \pm 0.5 \) THz. The vacf’s were multiplied by a windowing function prior to transformation, in order to suppress termination ripples.

Before considering the hydroxylated surface, we report calculations on an isolated water molecule, which provide both a check on our methods and a necessary reference point. The computational details were the same as already described, except that a cubic simulation box of 7 Å was used. Starting from the relaxed geometry, the ions were given random velocities in the plane of the molecule. The power spectra calculated at low temperature yielded frequencies in exact agreement with those found by harmonic analysis (table 1), and no appreciable anharmonic shift was found at 500 K.

To calculate the vibrational frequencies characteristic of the adsorbed species we started from the relaxed ionic configuration of the hydroxylated surface. A slight problem arises since we expect to find high-frequency modes associated with stretching of the O-H bonds, which will have little coupling to the other modes in the system. Therefore, after assigning random velocities to the ions we modified the relative velocity along the O-H bonds so that its magnitude corresponded to the average temperature, thus ensuring population of the high-frequency stretch modes. It is important to note that because the high-frequency modes are not in thermal equilibrium with the other modes, the measured power spectra do not represent a proper statistical average for the high frequencies,
although peak positions will be accurately given.

The power spectrum from a $120 \, \text{K}$ simulation is shown in figure 3. The contributions from terminal and bridging hydroxyls are shown separately. As well as the low-frequency vibrations of the slab, there are clearly several high-frequency modes, and an absence of any power around the $29 \, \text{THz}$ water bond-bending frequency. Notice that the sharp peak at $69 \, \text{THz}$ is associated with the terminal hydroxyl groups, and the broad, multipeak structure around $60 \, \text{THz}$ corresponds to bridging hydroxyl vibrations. The terminal hydroxyl mode frequency is very similar to those of the stretch modes in water. More surprising is the behaviour of the bridging hydroxyls: their slightly greater bond length suggests that their vibrations may be lower in frequency than the terminal hydroxyls, but quite obviously one cannot associate a single mode to their vibrations. Analysis of the ionic trajectories reveals that the broadening occurs because the hydrogen on the bridging hydroxyl interacts strongly with the terminal hydroxyl oxygen. The length of this hydrogen bond, and hence the strength of interaction, is largely determined by the low-frequency motions of the oxygen ions. These low frequency modes are well-coupled and consequently our concerns about the statistical accuracy of the high-frequency power spectrum do not apply here. In other words, the broadening of the bridging hydroxyl vibrational spectrum is not an artefact of the simulations. Using the correction factor of $1.61-1.67$, we estimate that the vibrational spectrum of the hydroxylated surface would exhibit a sharp peak between $111-115 \, \text{THz}$ (3800-3930 cm$^{-1}$), and a broad feature spanning $89-100 \, \text{THz}$ (2970-3330 cm$^{-1}$).

\section{Conclusions}

It is clear that dissociative adsorption on the fivefold Ti site is energetically favourable. Our simulations did not reveal any physisorbed state and therefore no barrier to dissociation, which is consistent with previous static calculations [20]. Thus, we predict that dissociation would occur at all temperatures; our dynamics is performed at $500 \, \text{K}$ in order to observe the reaction over a reasonably short simulation time.

We have not explicitly dealt with inter-molecular interactions in these calculations. Of course, the water molecule on the surface interacts with its periodic images, but the latter are at a fixed spacing and orientation with respect to the molecule. This means that the effects of hydrogen bonding between adja-
cent molecules cannot be investigated in our system. Thus, while the coverage is formally 0.5 ML, our results correspond more closely to the adsorption of a single molecule. Our finding dissociative adsorption in these circumstances is consistent with the results of Henderson [3] and Hugenschmidt et al [6] who both find dissociation at low coverages. Our adsorption energy may be slightly too high: applying Redhead [34] analysis to the observed TPD spectra [6, 20] indicates an energy of \( \sim 1 \) eV. There are a number of possible reasons for this discrepancy, including our use of \( \Gamma \)-point sampling, the absence of corrections for zero-point motion, the use of pseudopotentials, and the accuracy of density-functional theory.

An important conclusion from our work is that the vibrational spectrum of dissociated \( \text{H}_2\text{O} \) on \( \text{TiO}_2(110) \) does not contain two clear hydroxyl stretch mode frequencies. Rather, there is a sharp feature around the \( \text{H}_2\text{O} \) stretch frequencies associated with terminal hydroxyl modes, and a broad range of frequencies associated with the vibrations of bridging hydroxyls. This should provide important insight into the vibrational spectra observed in HREELS and other experiments. The broadening of the bridging hydroxyl frequencies is due to hydrogen bonding between the dissociation fragments.

Finally, we note that the experiments do indicate that there is molecular water adsorbed at monolayer coverage. Hugenschmidt et al [6] suggest that only 25\% of a monolayer of adsorbed water may be in dissociated form, while Henderson finds evidence of \( \text{H}_2\text{O} \) bond-bending vibrations in his HREELS spectra. We also note that static calculations [20] on the system studied here found a constrained physisorbed state only 0.3 eV above the dissociated state. Taking these things into account along with our results, we speculate that hydrogen bonding between hydroxyl groups and molecular water is sufficient to stabilise physisorption of the molecule, particularly if the bonding prevents the molecule from lying in the the (001) plane which we observed to be a precursor state to dissociation. It is also quite possible that such hydrogen bonding explains the discrepancy in our dissociation energy. It seems that inter-molecular interactions are of crucial importance in understanding the adsorption of water on \( \text{TiO}_2 \), and we hope to extend these calculations to address this problem in the near future.
Acknowledgments

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Tables

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Table 1: Calculated DFT-GGA harmonic frequencies for the three vibrational modes of water. The values obtained for two hydrogen masses $M_A$ are shown, along with the experimental values from reference [33].
**Figure captions**

**Figure 1:** Simulated system geometry. Light and dark spheres indicate titanium and oxygen ions respectively. (a) perspective view showing the slab geometry used. The 36-ion cell is extended for display purposes. (b) The 2 × 1 (110) surface cell of the simulated system: the two crystallographic unit cells are shown separated by a dotted line. The fivefold- and sixfold-coordinated titanium sites and the bridging oxygen site are labelled 5f, 6f and BO respectively.

**Figure 2:** Snapshots of the ionic configuration taken from a dynamical simulation of water dissociation. The red, yellow and grey spheres represent oxygen, titanium and hydrogen respectively. (a) Initial configuration in which the water molecule lies in the (T10) plane. See section 3 for descriptions of the other configurations.

**Figure 3:** Power spectra for the hydrogen ions in (a) the terminal hydroxyl and (b) bridging hydroxyl groups after water dissociation. The simulation was at 120 K. Note that the frequencies are shifted because of the use of a large hydrogen mass (see section 2). Note also the different y-scales used.