First-Principles Study of Adsorption of Dimethyl Methylphosphonate on the TiO₂ Anatase (001) Surface: Formation of a Stable Titanyl (Ti═O) Site

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ABSTRACT: Ab initio calculations have been performed to model the molecular adsorption of dimethyl methylphosphonate (DMMP) on the (001) surface of the anatase form of TiO₂. Both the relaxed unreconstructed (1 × 1) and the (4 × 1)-reconstructed clean surfaces have been analyzed. Adsorption occurs via a Ti—O═P dative bond to a coordinatively unsaturated surface Ti site. In both cases, one of the two Ti—O—Ti bridge bonds at the Ti adsorption site breaks leading to the formation of a stable Ti═O titanyl group. This species has not been reported in previous studies of adsorption on TiO₂ surfaces but is seen, in the present work, as an intermediate in the dissociative adsorption of H₂O.

1. INTRODUCTION

One of the many applications of titanium dioxide (TiO₂) is in the catalytic or photocatalytic destruction, through oxidation, of toxic chemicals. One important class of such species consists of organic reagents containing a P═O group, which constitute hazards to the environment and to personnel. Many of these are much too dangerous for routine experimentation; hence, relatively nontoxic simulants are used instead, the most significant of which is (CH₃)(CH₃O)₂P═O (dimethyl phosphonate, DMMP).

Due to the importance of this topic, there is a substantial amount of literature dealing with the interaction of DMMP with TiO₂, either in the dark or during photoexcitation of the TiO₂ to generate electron–hole pairs. Recent studies have also investigated the photocatalytic decomposition of actual toxic compounds on TiO₂. On an OH-free rutile (110) surface in ultrahigh vacuum (UHV), DMMP adsorption is molecular at room temperature and occurs via a Ti—O═P dative bond at a 5-fold-coordinated Ti₅c site. Figure 1 shows a model for the corresponding structure on anatase (101) and also identifies the Ti₅c, Ti₆c, and O₂c sites. The Ti₆c is 6-fold coordinated, and the O₂c is a 2-fold-coordinated O atom bridging Ti₅c and Ti₆c sites. For a given Ti₅c site, adjacent O₂c sites can be labeled as “nearest” (N) or “next-nearest” (NN) as illustrated in Figure 1. In addition to the dative bond, C—H—O₂c bonds form as indicated, based on the CH—O distances and C—H—O bond angles, and have been analyzed using the Atoms In Molecules (AIM) theory.

In contrast to the UHV experimental data, computational results for DMMP on OH-free rutile (110) and anatase (101) and (100) surfaces find that dissociation is energetically favored over molecular adsorption. It is noted here that the anatase (100) and (010) surfaces are isostructural, as are the (101) and (011) surfaces. For anatase (101), molecular adsorption is exothermic with an energy of ΔE_ads = −19.1 kcal/mol as obtained in a two-dimensionally periodic slab (2-DPS) calculation, whereas ΔE_ads = −25.0 kcal/mol is found for a possible first step in dissociation. Similar results for molecular vs. dissociative adsorption are found for the OH-free rutile (110) and anatase (100) surfaces.

Most of the experimental work in this area involves infrared spectroscopy and high-surface-area (HSA) powders for which anatase, rather than rutile, is usually the major constituent. Furthermore, the (101) face, which is the most stable surface for a bulk single crystal of anatase, makes only a small contribution to these powders. Here the (100) (or equivalently (010)) and (001) surfaces are dominant. In virtually all cases, the HSA powders are at least partially hydroxylated, and molecular adsorption on OH-terminated HSA TiO₂ can be seen only below ~214 K (refs 17 and 18). Above this temperature, reaction with OH occurs easily; although, DMMP does not react with liquid H₂O under normal conditions.

The fact that experiment shows predominantly molecular adsorption on OH-free rutile (110) but dissociative adsorption on hydroxylated HSA powders, together with the computational result that dissociation is energetically favored on OH-free surfaces, suggests that dissociation is kinetically limited in the absence of surface OH. It has been proposed that OH groups promote the first step in the reaction through nucleophilic attack on the P atom by the hydroxyl O atom, leading to formation of a P(OH)₂ bridge between Ti sites and either an adsorbed CH₃O group or free CH₃OH. Successive steps lead eventually to a tenacious PO₃ residue that poisons further...
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Ab initio calculations have been performed to model the molecular adsorption of dimethyl methylphosphonate (DMMP) on the (001) surface of the anatase form of TiO2. Both the relaxed unreconstructed (1 1)- and the (4 1)- reconstructed clean surfaces have been analyzed. Adsorption occurs via a Ti?OdP dative bond to a coordinatively unsaturated surface Ti site. In both cases, one of the two Ti-O-Ti bridge bonds at the Ti adsorption site breaks leading to the formation of a stable TidO titanyl group. This species has not been reported in previous studies of adsorption on TiO2 surfaces but is seen, in the present work, as an intermediate in the dissociative adsorption of H2O.
catalytic activity. A recent study\textsuperscript{30} of the adsorption of (CH$_3$)$_2$(OH)P=O (methylphosphonic acid, MPA) on OH-free rutile TiO$_2$ (110) combining scanning tunneling microscopy in UHV and ab initio computation found that dissociation to form a (CH$_3$)$_2$P(=O)(−O−Ti$_{5c}$)$_2$ bridge and two OH sites occurs spontaneously at room temperature. However, such a process may be less likely for DMMP, in which the two OH groups of MPA are replaced by CH$_3$O.

The purpose of the present work is to investigate the adsorption of DMMP on the OH-free anatase (001) surface that, together with the anatase (100), is the major constituent in most HSA TiO$_2$ powders. This is a necessary preliminary to achieving an understanding of the effects of OH on the adsorption and dissociation of DMMP on different TiO$_2$ surfaces. The (001) surface is also known to exhibit a high degree of photocatalytic activity.\textsuperscript{31} It will be seen that molecular adsorption of DMMP on anatase (001) is distinctly different from that on other TiO$_2$ surfaces. On the relaxed but unreconstructed (001)-(1 × 1), as well as on the more stable (4 × 1)-reconstructed surface, adsorption of DMMP leads to an extensive rearrangement of surface atoms not seen for other TiO$_2$ surfaces.

\section{RESULTS}

\subsection{Adsorption on the (1 × 1) Surface.} The ideally terminated (001) surface (Figure 2a) is nonporal and stoichiometric, with one O$_{2c}$ and one O$_{3c}$ for every Ti$_{5c}$. It is also autocompensated since the excess electron density on the Ti$_{5c}$ is transferred to the electron-deficient O$_{2c}$ to give a closed-shell configuration on both. However, recent results\textsuperscript{45} show that relaxation is not complete on the (001)-(1 × 1) surface and that there are occupied surface states in the band gap very close to the valence band maximum (VBM). An alternative termination, in which the O$_{2c}$ layer is removed to give a surface consisting of Ti$_{4c}$ and O$_{3c}$ sites, is neither stoichiometric nor autocompensated and is expected to be much less stable.

Table 1 shows the structural changes resulting from relaxation. These consist largely of displacements of O atoms in the first and second O−Ti−O trilayers in opposite directions along the [100] axis, together with an outward displacement of O$_{2c}$ atoms ("O1" in Table 1) along the surface normal.\textsuperscript{35,43,44} The Ti$_{5c}$ atoms ("Ti1" in Table 1) also undergo displacements opposite to those of O$_{2c}$, resulting in short and long Ti$_{5c}$−O$_{2c}$ bonds. As is seen in Table 1, displacements beyond the first Ti and third O layers are very small; however, the displacements in the outermost layers lead to a large tensile stress, which is relieved by the (4 × 1) reconstruction,\textsuperscript{45} described in Sec. 3.3, or by adsorption\textsuperscript{36,46}.

Figure 2b shows the starting structure for molecular adsorption of DMMP on the relaxed (1 × 1) surface. It has previously been shown\textsuperscript{24,25} that Ti−O=P bonding at a coordinatively unsaturated Ti site is the most favorable mechanism for adsorption and that bonding to a methoxy O atom is negligible. Previous work\textsuperscript{25} also shows the formation of C−H−O$_2$c hydrogen bonds and analyzes these using the AIM theory. Examination of Figure 2b shows that initial structures differing by a rotation of DMMP conformation was the one identified\textsuperscript{40,41} as the lowest in energy for the gas-phase molecule.

Two different computational approaches were employed in order to verify the lack of a significant influence on the final results. In the first, relaxation was done at the restricted Hartree−Fock (RHF) level, followed by a total-energy calculation using density functional theory (DFT). In the second, the entire calculation was performed using DFT. In both cases, DFT employed the B3LYP functional, the applicability of which to studies of the adsorption of organic species on TiO$_2$ has been discussed elsewhere.\textsuperscript{32} During relaxation, the atoms in the lowermost O−Ti−O trilayer were frozen in the optimized bulk-lattice positions obtained previously\textsuperscript{25} while all other Ti$_{5c}$ and DMMP atoms were unconstrained. Geometry optimizations used an effective-core pseudopotential for Ti and a modified 6-31G(d) basis set for O, as previously described.\textsuperscript{24,25} The DFT energy calculations for the relaxed structures used the all-electron basis sets for Ti and lattice O, also as previously described.\textsuperscript{24,25} The 6-31G(d,p) basis sets appropriate to the free molecule were used for DMMP since larger molecular basis sets led to linear-dependency problems in 2-DPS calculations.\textsuperscript{24,25} Due to the large supercell size, all calculations used a (1 × 1) Monkhorst-Pack grid. Other computational parameters including the convergence criteria for geometry optimization, the definition of adsorption energy (ΔE$_{ads}$) and the correction for basis set superposition error (BSSE) are described elsewhere.\textsuperscript{24,25} The basic approach outlined above was tested in several ways as described in the following two sections.
about the PdO bond are inequivalent due to the presence of short and long Ti5c-O2c bonds. The various structures differ as to whether C—H---O2c bonds form to short- or long-bonded O2c atoms. It has also been shown24,25 that C—H---O2c bonding tends to “lock” the DMMP in whatever rotational orientation is selected initially. Thus the relaxed structure may represent only a local, and not a global, energy minimum. In the present work, initial configurations in which the DMMP was rotated by 90 or 180° about the PdO bond, relative to that shown in Figure 2b, were considered; although, only the structure shown was relaxed all the way to convergence. This geometry appears to be the most stable, but the differences among the relaxed energies are very small (<2 kcal/mol). More importantly, the unusual relaxed structure described below was seen for all three starting configurations. The initial structure in Figure 2b shows the Ti---OP bond at an angle with respect to the surface normal. An initial structure with the Ti---OP bond along the surface normal relaxed into the configuration shown at an early stage in the optimization.

Relaxation (Figure 2c) leads to a breaking of the long Ti5c—O2c bond at the adsorption site, with the terminal O atom then

Figure 2. (a) The ideally terminated anatase (001) surface. The outermost Ti (O) atoms are 5-fold (2-fold) coordinated, and the Ti and O sites referred to in Table 1 are labeled. (b) The relaxed (001) surface with adsorbed molecular DMMP before further relaxation. “Short” and “long” Ti5c—O2c bonds (cf. Table 1) are labeled. (c) Same as (b) but after relaxation following adsorption of DMMP. The Ti≡O site is labeled, and the dashed lines indicate possible H-bonds identified on the basis of the CH---O distances (2.22 to 2.55 Å) and C---H---O bond angles (139° to 162°).

Table 1. Comparison of Calculated Atomic Displacements Due to Relaxation of the Anatase (001)-(1 × 1) Surface

<table>
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<td>146.7°</td>
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* All distances are in Angstroms. The first (second) number gives the displacement along the [100] ([001]) direction. All displacements along [010] are zero. See Figure 2 for definitions of atoms and axes. O1 is a 2-fold-coordinated O2c atom. All other O atoms are 3-fold-coordinated O3c sites. Similarly, Ti1 is a Ti5c, while all other Ti atoms are Ti6c. Optimization using RHF with ECPs. Optimization using DFT with the B3LYP functional and ECPs. DFT plane-wave/pseudopotential calculation; 6 O—Ti—O trilayers; PBE functional. DFT calculation; Bloch functions constructed from localized Gaussian basis sets; 10 O—Ti—O trilayers; B3LYP functional. These values refer to the “short” and “long” Ti5c—O2c bond lengths. The ideally terminated value is 1.936 Å in the present work. This is the bond angle at the surface O2c site. The ideally terminated value is 155.2° in the present work.
forming a Ti=O bond with its remaining neighbor. This interpretation is based on the Ti=O distance of 1.634 Å, which is much less than the computed bulk Ti—O distance of 1.967 Å (1.936 Å) parallel (perpendicular) to the [001] axis. The Ti atoms at the Ti=O and DMMP sites relax away from each other in the [100] direction by about −0.66 and +0.36 Å, respectively, relative to the positions on the bare relaxed surface. The O2c atoms bonded to these Ti sites also displace along [100] by about 0.36 Å away from the adsorption site. The Ti in the Ti=O and the remaining O2c to which it is bonded also displace outwardly along the surface normal by about 0.25 and 0.18 Å, respectively. Most of these displacements can be seen qualitatively in Figure 2c. Other atoms exhibit smaller displacements (generally <0.05 Å) in all directions, including [010]. Due to the large displacements in the vicinity of the adsorption site the (4 × 4) supercell may not be sufficiently large to permit complete relaxation, and the \( \Delta E_{ads} \) value given below must therefore be considered a lower-limit estimate of the low-coverage adsorption energy. Similar considerations affect \( \Delta E_{ads} \) for the dissociative adsorption of \( \text{H}_2\text{O} \) (see Section 3.2).

The formation of a titanyl Ti=O site is an unusual and unanticipated result. Previously such species (with a bond length of 1.62 Å) were proposed to form on the rutile (011)-(2 × 1) surface. However, recent work has found that other structures, not involving Ti=O, are more stable for that surface. The (001) surfaces of oxides with the M2O3 corundum structure (M = V, Cr, Fe) have been shown both experimentally and theoretically (ref 49 and works cited) to form M = O sites. However, to the best of our knowledge there are no prior reports of Ti=O formation in response to adsorption on a TiO2 surface. Many other computational studies of reactive species adsorbing on anatase (001) have also observed the breaking of a Ti4c—O2c bond. However, the reagents involved (\( \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{etc.} \)) are all able to release an H atom, which reacts with the singly coordinated O to form a Ti—OH site instead of a Ti=O. The subject of \( \text{H}_2\text{O} \) adsorption is discussed further in Section 3.2. The Ti—O=P bond is characterized by Ti—O and O=P lengths of 1.962 and 1.500 Å respectively and an angle of 163°. The P=O distance is 0.041 Å longer than that computed for the free molecule. After BSSE correction a DFT adsorption energy of \( \Delta E_{ads} = −42.5 \text{ kcal/mol} \) was found. The correction, \( \Delta E(\text{BSSE}) = 6.6 \text{ kcal/mol} \), was obtained from previous 2-DPS calculations for molecular adsorption of DMMP on anatase (101) and (100) surfaces using the same methods and basis sets as those employed here.

Another issue, which relates to the experimental detection of Ti=O (see Section 3.4 below), is whether it persists after removal of adsorbed DMMP. It was found that, with DMMP removed, the long Ti5c—O bond does not reform but instead the Ti=O remains intact with some additional relaxation, consisting of a small (<0.2 Å) displacement inward along the surface normal and toward the vacant adsorption site. The resulting energy is 5.0 kcal/mol lower than that of the relaxed (1 × 1) surface, which represents the exothermic formation energy of the Ti=O. Subtracting this from \( \Delta E_{ads} \) gives an estimate of −37.5 kcal/mol for the Ti—O=P bond energy, which can be compared with values of −21.0 and −19.1 kcal/mol respectively for molecular adsorption on the (100) and (101) anatase surfaces. This trend parallels that in surface energy 35,50 (\( \sigma = 0.90, 0.53, \) and 0.44 J/m² respectively for (001), (100), and (101)), which indicates that the Ti—O=P bond energy decreases with increasing surface stability (i.e., decreasing \( \sigma \)). The rutile (110) surface also fits this pattern, with \( \Delta E_{ads} = −17.6 \text{ kcal/mol} \) and \( \sigma = 0.31 \text{ J/m}^2 \).

### 3.2. Test Calculations

Several tests were done to validate the procedures described above and to demonstrate that the Ti=O is not an artifact of the calculation. Those involving different initial configurations for adsorbed DMMP have been described in the previous section. Geometry optimizations for adsorbed DMMP using RHF vs DFT, as described in Section 2, were compared, and the differences in atomic displacements were negligibly small (∼5% or less). The BSSE-corrected \( \Delta E_{ads} \) for the relaxed structures (both obtained in single-point DFT calculations with all-electron basis sets) were −42.5 vs −40.3 kcal/mol. A similar comparison for the bare (1 × 1) surface has been discussed already (cf. Table 1). In another test, RHF geometry optimization was done for a different 2-DPS model, one with eight O—Ti—O trilayers, a (3 × 3) supercell and DMMP placed symmetrically on both surfaces so as to maintain the center of inversion of the supercell. All atoms were unconstrained in the relaxation, and the same structure as described above, including the Ti=O site, was obtained.

Finally, the adsorption of \( \text{H}_2\text{O} \) was considered. Several DFT plane-wave/pseudopotential calculations 38,39,46,50,51 have found that, at low coverage, \( \text{H}_2\text{O} \) dissociates spontaneously on the anatase (001) surface. This is accompanied by the breaking of a Ti5c—O2c bond and the formation of an H-bonded pair of Ti5c—OH sites with \( \Delta E_{ads} \) in the range of −32 to −39 kcal/mol. \( \Delta E_{ads} \) decreases significantly with increasing coverage 36,46,50,51, which may indicate a repulsive interaction due to the large atomic displacements in the vicinity of an adsorption site. This calculation was repeated, using the same model and methods as employed for DMMP, beginning with \( \text{H}_2\text{O} \) adsorbed molecularly at a Ti5c site on the relaxed (1 × 1) surface (Figure 3a). The \( \text{H}_2\text{O} \) was adsorbed via a Ti—O bond with the 2-fold axis normal to the surface and with the plane of the molecule lying in the [010] plane. The coverage was one \( \text{H}_2\text{O} \) per (4 × 4) supercell, i.e., one \( \text{H}_2\text{O} \) per 16 surface Ti5c sites, but one per 4 Ti5c sites on the [100] axis along which most of the relaxation occurs. Early in the relaxation (within 6 optimization steps) the long Ti5c—O2c bond broke, and a Ti=O bond formed with a minimum interatomic distance of 1.650 Å (Figure 3b). Continued relaxation led to the transfer of an H to form a Ti—OH, resulting in the same H-bonded pair of Ti—OH sites as previously reported (Figure 3c). Thus the Ti=O site is found to be an intermediate in the dissociative adsorption of \( \text{H}_2\text{O} \).

### 3.3. Adsorption on the (4 × 1) Surface

The atomically clean anatase (001) surface is known from experiment to exhibit a (4 × 1) reconstruction. 52–54 Ab initio modeling 45 shows that this is driven by the large reduction in surface energy that follows from the decrease in the tensile stress intrinsic to the (1 × 1) surface. Figure 4a shows the ad-molecule (ADM) structure in which one of four O2c rows in the [010] direction (cf. Figure 2) is replaced with TiO3 units to form three O2c and one Ti4c site per (4 × 1) unit cell. The increase in energy due to the addition of coordinatively unsaturated surface atoms is more than offset by the relaxation of the remaining Ti5c—O2c bonds to “normal” lengths. As expected, a Ti4c ridge site is found experimentally 37,56 and computationally 37,46 to be more reactive than a Ti5c terrace site. In particular, spontaneous dissociation of \( \text{H}_2\text{O} \) to form two Ti—OH groups has been reported 37,53 to occur at Ti4c ridge sites but not at Ti5c terrace sites. It is noted that formation of the (4 × 1) reconstruction requires annealing at high temperature (∼1050 K, ref 52) and might not occur at the lower temperatures typically used in studies employing HSA powders. Hence, the results described above for the (1 × 1) surface remain relevant.
Following previous studies of adsorption on the (001)-(4 × 1) surface, the model used here is asymmetric, with reconstruction on only one slab surface and the other held fixed with atoms in the ideal bulk-lattice positions (cf. Section 2).

The surface bond lengths obtained for the bare (4 × 1) surface agreed well with, but were about 1% smaller than, those previously reported. A small fraction of this difference is due to the slightly smaller bulk [100] lattice constant (a = 3.781 vs 3.786 Å) used in the present work. The Ti–O bond lengths of 1.965 and 1.974 Å are close to the computed bulk Ti–O bond lengths of 1.936 and 1.967 Å. Figure 4b shows the relaxed structure for adsorbed DMMP, which, similarly to the (1 × 1) result, exhibits the breaking of a Ti–O bridge and the formation of a Ti–O site with a bond length of 1.637 Å. Since the Ti–O Ti is then 5-fold coordinated, the stabilization of this structure is thought to result from the decrease in the degree of coordinative unsaturation. A BSSE-corrected $\Delta E_{\text{ads}}$ of $-58.4$ kcal/mol was obtained. In agreement with previous work, $\Delta E_{\text{ads}}$ at a Ti site is significantly higher than at a (1 × 1) Ti site. As in the case of the (1 × 1) surface, relaxation after removal of adsorbed DMMP led to the continued presence of the Ti–O site. However, the energy in this case was only slightly lower, by 1.3 kcal/mol, than that of the bare relaxed (4 × 1) surface.

3.4. Experimental Observables. Techniques that may be suitable for detecting Ti–O are vibrational spectroscopy, ultraviolet photoemission spectroscopy (UPS), and scanning tunneling spectroscopy (STS). Although the $\nu$(Ti–O) stretching-mode frequency has not been obtained in the present work, experiment shows that the corresponding modes for V=O, Cr=O, and Fe=O on the (0001) surfaces of $\text{M}_2\text{O}_3$ oxides all occur in the 990–1040 cm$^{-1}$ (123–129 meV) range. Observation of $\nu$(Ti–O) in the presence of adsorbed DMMP would be complicated by the strong DMMP absorption band near 1032 cm$^{-1}$. However, the results discussed above show that the Ti–O persists after removal of the DMMP. Hence, $\nu$(Ti–O) might be observable if DMMP can be desorbed under conditions that do not also eliminate the Ti–O. Experiment shows that molecular desorption of DMMP, accompanied by some decomposition, occurs at about 440 K for rutile (110). However, $\Delta E_{\text{ads}}$ for DMMP on this surface is only $-17.6$ kcal/mol (ref 25), which is significantly lower than on the anatase (001). Thus, it remains to be seen whether DMMP can be thermally desorbed from the (001) surface without removing the Ti–O. Another potential difficulty in vibrational spectroscopy is the presence of the anatase transverse-optic (TO) phonon at 838 cm$^{-1}$. The width and intensity of the TO phonon peak might partially obscure $\nu$(Ti–O) in an infrared reflection–absorption or a high-resolution electron energy loss experiment.
In the model originally proposed for the rutile (011)-(2 × 1) surface, Ti≡O produces a narrow feature in the density of states, not seen for other stoichiometric TiO$_2$ surfaces, at 1 eV below the VBM. Similar features are seen in the computed (1 × 1) density of states (DOS) shown in Figure 5 and have been assigned using the partial DOS for individual atoms. These results were obtained after relaxing the surface following removal of adsorbed DMMP, and the Monkhorst-Pack grid was increased to $(4 \times 4)$ for computation of the DOS. The main contribution from the Ti≡O bond is in Peak 1, at ~0.45 eV below the bulk VBM, which falls on top of structure derived from other atoms. There is also some Ti≡O contribution to Peak 2, but a large part of the density here is derived from surface O$_{2c}$ atoms. A similar Peak 1, although much less pronounced, is found for the (4 × 1) surface after removal of DMMP (not shown). Here again the features of interest may be obscured in UPS or STS by structure due to adsorbed DMMP. However, the same remarks about the removal of DMMP, made in connection with $\nu$(Ti≡O), also apply here.

No empty states localized on the Ti≡O were found in the DOS at or below the conduction band minimum (CBM, not shown). Hence, Ti≡O might not easily be detected using electron energy-loss spectroscopy (ELS) as a probe of electronic excitations associated with this site. Such empty states are seen at about 1.5 to 2.5 eV above the CBM, and ELS transitions involving the Ti≡O might be obscured by stronger interband excitations.

4. CONCLUSIONS

The molecular adsorption of DMMP on the OH-free TiO$_2$ (001)–(1 × 1) and (4 × 1) surfaces was modeled using ab initio calculations. The adsorption is exothermic, with $\Delta E_{\text{ads}}$ of ~42.5 and ~58.4 kcal/mol, respectively. Relaxation leads to the breaking of the long Ti$_{5c}$–O$_{2c}$ bond in the case of the (1 × 1) surface, or a Ti$_{4c}$–O$_{2c}$ bond in the case of the (4 × 1), and the formation of a Ti≡O bond at a neighboring Ti site. To the best of our knowledge, Ti≡O formation in response to adsorption has not previously been reported for any TiO$_2$ surface. Results presented here for H$_2$O adsorption on the (1 × 1) surface suggest that a Ti≡O intermediate is important in dissociative chemisorption, and consequent Ti–OH formation, for species with one or more labile H atoms. It is speculated that other adsorbates (e.g., acetone), which might form a dative bond to a Ti$_{4c}$ or Ti$_{5c}$ without decomposing to form Ti–OH, could also produce a stable Ti≡O site. Also, a well-chosen alternative to DMMP would not interfere with spectroscopic detection of the Ti≡O, thus making desorption unnecessary. However, a “strong” dative bond may be required for Ti≡O formation to occur. For example, a recent study$^{60}$ of thiophene adsorption on anatase (001)–(1 × 1) via a Ti$_{4c}$–S dative bond, with a $\Delta E_{\text{ads}}$ of only ~5.4 kcal/mol, shows no breaking of the Ti$_{4c}$–O$_2$–Ti$_{4c}$ bridge and hence no Ti≡O formation. The implication is that a sufficiently strong adsorption bond to the Ti$_{4c}$ weakens the long Ti$_{4c}$–O$_2$ bond enough to overcome the barrier to breaking this bond and forming the Ti≡O. The existence of such a barrier would account for the fact that Ti≡O does not form spontaneously during relaxation of the bare surface.

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**Figure 5.** Total DOS, for all atoms in the 2-DPS supercell, for the (1 × 1) surface after removal of adsorbed DMMP and subsequent relaxation. The labeled features receive contributions from the Ti≡O bond. The zero of energy is at the bulk valence band maximum.

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