# Insights into Photoexcited Electron Scavenging Processes on $TiO_2$ Obtained from Studies of the Reaction of $O_2$ with OH Groups Adsorbed at Electronic Defects on $TiO_2(110)$

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In this study we show that molecular oxygen reacts with bridging OH  $(OH_{br})$  groups formed as a result of water dissociation at oxygen vacancy defects on the surface of rutile  $TiO_2(110)$ . The electronic structure of an oxygen vacancy defect on  $TiO_2(110)$  is essentially the same as that of electron trap states detected on photoexcited or sensitized TiO<sub>2</sub> photocatalysts, being Ti<sup>3+</sup> in nature. Electron energy loss spectroscopy (EELS) measurements, in agreement with valence band photoemission results in the literature, indicate that water dissociation at oxygen vacancy sites has little or no impact on the electronic structure of these sites. Temperature programmed desorption (TPD) measurements show that O<sub>2</sub> adsorbed at 120 K reacts with near unity reaction probability with  $OH_{br}$  groups on  $TiO_2(110)$  to form an unidentified intermediate that decomposes to generate terminal OH groups at nondefect sites. Commensurate with this process, the electronic defect associated with the original oxygen vacancy defect  $(Ti^{3+})$  is oxidized. Vibrational EELS results indicate that the reaction between O<sub>2</sub> and OH<sub>br</sub> occurs at about 230 K, whereas electronic EELS results suggest that charge is transferred away from the vacancies at 90 K. Detailed TPD experiments in which the precoverage of water was varied indicate that chemisorption of  $O_2$  at cation sites on the TiO<sub>2</sub>(110) surface is not required in order for the reaction between  $O_2$  and  $OH_{br}$  to occur, which implies a direct interaction between weakly bound (physisorbed)  $O_2$  and the OH<sub>br</sub> groups. In agreement with this conclusion, we find that second-layer water, which selectively hydrogen-bonds to bridging  $O^{2-}$  sites and bridging OH groups, blocks the reaction of  $O_2$  with  $OH_{br}$  groups and prevents oxidation of the vacancy-related  $Ti^{3+}$  electronic state. These results suggest that the electron scavenging role of  $O_2$  in photocatalysis may involve a direct reaction between  $O_2$  and trapped electrons located at bridging OH groups. Our studies suggest that the negative influence of high water concentrations in gasphase heterogeneous photocatalysis studies results from hydrogen-bonded water blocking access of  $O_2$  to trapped electrons located at surface OH groups.

### 1. Introduction

The primary role of molecular oxygen in photooxidation of organic molecules over TiO<sub>2</sub> photocatalysts is to scavenge photoexcited electrons that would otherwise deactive the photocatalyst by negative charge accumulation.<sup>1–5</sup> The species resulting from this electron scavenging process are typically assigned to  $O_2^-$  or HO<sub>2</sub>.<sup>6–12</sup> These species may also play a direct role in oxidation of organics.<sup>1–3,13–15</sup> Formation of HO<sub>2</sub> requires the presence of water/OH. Fu et al.<sup>16</sup> recently reviewed the literature on the role of water in photocatalysis over TiO<sub>2</sub>, and there appears to be much speculation about the role of water/ OH in photochemical processes on TiO<sub>2</sub>.

It is generally held that  $O_2$  scavenges photoexcited electrons from the TiO<sub>2</sub> conduction band (CB); recent research<sup>4,17–20</sup> suggests that the photoexcited electrons are first trapped in shallow band gap states on the subpicosecond time scale prior to any O<sub>2</sub>-related chemistry. Measurements of the trapped electron lifetimes have ranged from picoseconds to minutes<sup>7,17,20–24</sup> depending, in part, on whether electron acceptors (such as O<sub>2</sub>) are present. The electron trap states on TiO<sub>2</sub> can also be populated by photoexcited electron transfer from an adsorbed sensitizer, such as a dye molecule<sup>9,25–31</sup> or a narrow band gap semiconductor particle.<sup>32,33</sup> Several groups<sup>7,8,12,24,26,32,34–36</sup> have observed that electron trap states susceptible to scavenging by O<sub>2</sub> are located at the surface of TiO<sub>2</sub> as Ti<sup>3+</sup>-related sites.

The ability of oxygen to scavenge photoexcited electrons has been shown to resemble the reaction of oxygen with thermally generated electronic defects on anatase and rutile. For example, Anpo et al.<sup>6</sup> found that the EPR signature of  $O_2^-$  formed after photoexcitation of O<sub>2</sub> adsorbed on a polycrystalline TiO<sub>2</sub> film was the same as that observed in the dark after exposure of O2 to the thermally activated film. The thermal stability of  $O_2^-$  in both cases was the same, with the  $O_2^-$  EPR signal absent after heating to 423 K. Jenkins and Murphy37 recently observed that the same  $O_2^-$  species (on the basis of EPR data) forms at 100 K on both thermally annealed and UV irradiated rutile TiO<sub>2</sub> surfaces. Kormann et al.35 also observed that the interactions of O<sub>2</sub> with anatase and rutile under UV illumination were similar to the O<sub>2</sub>/TiO<sub>2</sub> interactions observed for thermal activation in the dark. In both cases (light and thermal activation), the authors proposed that  $O_2$  reacted with Ti<sup>3+</sup> surface sites to make HO<sub>2</sub> species. In the photoexcitation case, the Ti<sup>3+</sup> sites were formed from photoexcited electron trapping, whereas in the thermal activation case these sites were formed from reduction of the

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surface. We recently showed that  $O_2$  adsorption at low temperature on "thermally activated" rutile TiO<sub>2</sub>(110) results in formation of  $O_2^-$  species at oxygen vacancy sites.<sup>38,39</sup> The formation of this species at oxygen vacancies on TiO<sub>2</sub>(110) has also been modeled by de Lara-Castells and Krause<sup>40,41</sup> using periodic ab initio Hartree–Fock calculations. Our studies show that the  $O_2^-$  species is stable on the surface up to 410 K, at which point it desorbs as  $O_2$ . This is in general agreement with the stability of  $O_2^-$  observed via EPR by Anpo et al.<sup>6</sup>

In this study, we examine how water influences the interaction of  $O_2$  with electrons trapped at oxygen vacancies on TiO<sub>2</sub>(110) in an effort to better understand the electron scavenging role of  $O_2$  in photocatalysis on TiO<sub>2</sub>. Our results show that  $O_2$  "titrates" both charge and hydrogen atoms associated with bridging OH (hereafter referred to as "OH<sub>br</sub>") groups associated with water dissociation at oxygen vacancy sites on TiO<sub>2</sub>(110). However, hydrogen-bonding of a water molecule to these bridging OH blocks the ability of  $O_2$  to reaction with the OH groups and to scavenge the electrons associated with defect.

#### 2. Experimental Section

Experiments in this study were performed in two separate UHV systems,<sup>42,43</sup> using TiO<sub>2</sub>(110) crystals from several different vendors (First Reaction, Marketech International, Commercial Crystal Growers, and Princeton Scientific). Data obtained from this distribution of crystals were consistent with each other, indicating that any vendor-specific variations in crystal quality did not noticeably impact the surface chemistry of water on TiO<sub>2</sub>(110). The as-received crystals were mounted in a manner described previously,44 cleaned by Ar<sup>+</sup> ion sputtering and annealing in UHV at 850 K. No contaminants were detected by Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS) after the sputter/anneal treatments. Furthermore, a sharp  $(1 \times 1)$  pattern was routinely observed in low energy electron diffraction (LEED) after annealing. Signatures of the presence of surface oxygen vacancies were evident in temperature programmed desorption (TPD), electron energy loss spectroscopy (EELS) and XPS after bulk reduction of the crystal to a light blue color. The surface oxygen vacancy population varied depending mostly on the level of bulk reduction, which more-or-less tracked the intensity of the crystal's blue color and was used as a rough indicator of the level of bulk reduction.45 The exact relationship between the level of bulk reduction and the surface vacancy population on TiO<sub>2</sub>(110) has not yet been addressed in the literature. However, Jenkins and Murphy<sup>37</sup> have correlated the relative concentration of  $Ti^{3+}$  in the bulk and surface of  $TiO_2$  powders using EPR as a function of annealing temperature in a vacuum. These authors found that as the annealing temperature was increased, the ratio of bulk-to-surface Ti<sup>3+</sup> increased from about 0.05 at 773 K to about 0.5 at 1073 K. For TiO<sub>2</sub>(110), the progression toward increasing levels of bulk reduction results in the surface reconstructing to form a  $(1 \times 2)$  structure that possesses Ti<sub>2</sub>O<sub>3</sub>like features (see refs 46 and 47 and references therein) instead of forming additional vacancies. The level of bulk reduction at which this occurs is not known; however the  $(1 \times 2)$  surface was not observed on any of the  $TiO_2(110)$  crystals used in this study.

The oxygen vacancy population for each crystal (at its respective point in the bulk reduction "life cycle" of TiO<sub>2</sub>) was easily calibrated using H<sub>2</sub>O TPD, as discussed in previous studies.<sup>39,48–50</sup> For each TPD experiment (unless otherwise stated), the crystal was annealed in UHV at 850 K for 10 min and subsequently exposed at 90–120 K to research-grade purity



**Figure 1.** H<sub>2</sub>O TPD spectrum (m/e = 18) obtained after exposure of approximately 1.4 ML of H<sub>2</sub>O at 120 K to TiO<sub>2</sub>(110) with 14% oxygen vacancy sites. The "filled" spectrum results from the same conditions except that the water adlayer was preheated to 370 K and recooled to 120 K prior to performing TPD.

gases. Gases were typically exposed to the  $TiO_2(110)$  surface using a directional doser, which minimized background effects. In some experiments, oxygen or water was dosed by backfilling the chamber. H<sub>2</sub>O was purified using liquid nitrogen (LN2) freeze-pump-thaw cycles, and O<sub>2</sub> was passed through a LN2 trap prior to being dosed. TPD spectra from both chambers were performed with a 2 K/s ramp. Vibrational (HREELS) and electronic (EELS) electron energy loss measurements were performed in the specular scattering geometry with primary electron beam energies of 8 and 20-25 eV, respectively. No electron-induced decomposition was observed during these experiments. The flux of electrons at the sample in these experiments was on the order of 0.1 nA, which is insignificant to produce detectable levels of electron-induced decomposition products during the course of the electron energy loss measurements. (At an incident flux of 0.1 nA and an assumed DEA cross section of 10<sup>-16</sup> cm<sup>2</sup> for water, it would require approximately 20 days of continual electron exposure to accumulate 0.1 monolayer of electron-induced decomposition products.) All electron energy loss spectra were recorded at 120 Κ.

## 3. Results and Discussion

**3.1. Interaction of Water with Oxygen Vacancies on TiO**<sub>2</sub>-(**110**). Figure 1 shows TPD data for a 1.4 ML coverage of water adsorbed at 120 K on a TiO<sub>2</sub>(110) surface possessing about 14% oxygen vacancy sites. (One monolayer (ML) equals  $5.2 \times 10^{14}$ sites per cm<sup>2</sup>.) Features at 178 (off scale), 270 and 520 K are assigned to desorption from the second layer, the first layer and oxygen vacancy sites, respectively. The former two TPD states result from molecularly adsorbed water hydrogen-bonded to bridging oxygen sites and chemisorbed at nondefect cation sites, respectively, whereas the 520 K TPD state is from water



**Figure 2.** EELS spectra from the interaction of water and oxygen on  $TiO_2(110)$  with 14% oxygen vacancy sites: (a) the clean surface; (b) multilayer H<sub>2</sub>O; (c) 1 ML of H<sub>2</sub>O; (d) 1 ML of H<sub>2</sub>O after preheating to 370 K; (e) 1 ML of H<sub>2</sub>O after preheating to 590 K; (f) 1 ML of H<sub>2</sub>O after exposure to O<sub>2</sub> at 700 K. All spectra were recorded in the specular direction at 120 K with an electron beam energy of 25 eV. Spectra are displaced vertically for clarity.

dissociatively adsorbed at vacancies.<sup>48–50</sup> (Nondefect sites on TiO<sub>2</sub>(110) are inactive for water dissociation under UHV conditions.<sup>44,48,51–54</sup>) Water dissociation at vacancies results in two bridging OH<sub>br</sub> groups per each vacancy site. One of these OH<sub>br</sub> groups can be thought of as comprising oxygen from the water molecule adsorbed at the vacancy, whereas the second results from hydrogen transfer to a neighboring bridging oxygen anion site (O<sup>2–</sup><sub>br</sub>). In principle, these two OH<sub>br</sub> groups are indistinguishable. The coverage in the 520 K H<sub>2</sub>O peak, compared to that in the 270 K state, provides an accurate measure of the surface oxygen vacancy population. A surface possessing only dissociative water at vacancies can be prepared by preheating a multilayer exposure of water to 370 K, as shown by the filled spectrum in Figure 1.

We examined the interaction of water with oxygen vacancies using EELS to address the issue of whether the electronic structure of vacancies is influenced by water/OH<sub>br</sub>. Figure 2 shows EELS data for the interaction of water with a  $TiO_2(110)$ surface possessing about 14% oxygen vacancy sites. The EELS spectrum for the clean surface is shown in Figure 2a. Loss intensity above 3.4 eV, which peaks at about 5.2 eV, is associated with the band-to-band transition in the TiO<sub>2</sub>(110) surface, whereas the nearly as intense loss feature at about 0.9 eV is from excitation of the shallow band gap state associated with oxygen vacancies. The intensity of the 0.9 eV loss, in comparison with the band-to-band transition intensity, indicates that the excitation probability of the defect state (with 25 eV electrons) is considerably greater than that of the band-to-band transition. This is consistent with the 0.9 eV loss resulting from excitation of a polaron state.55-58 These results are also consistent with photoemission studies by numerous groups.<sup>59</sup> The valence band photoemission signature of surface oxygen

vacancies is an occupied band gap state located at about 0.8 eV below the Fermi level (which is close to the CB edge).<sup>60</sup> This energy position is in the range observed for the position of electron trap states generated via direct photoexcitation of TiO<sub>2</sub> or via charge transfer to TiO<sub>2</sub> from a photoexcited sensitizer. Photoelectrochemical measurements place the potential energy of these surface Ti<sup>3+</sup>-related electron trap states between 0.5 and 0.8 eV below the TiO<sub>2</sub> CB edge,<sup>21,27,31,61-63</sup> whereas transient photoabsorption studies place the position at about 2 eV below the CB edge on the basis of observations of a broad absorption feature at about 600-650 nm.<sup>7,24,32,34,64,65</sup> The latter studies assume that excitation of trapped electrons is to the  $TiO_2$  CB edge. However, given that the first maximum in Ti 3d density of states (for rutile) is located at about 1 eV above the CB edge,<sup>66</sup> the position of the trapped electron states as derived from these optical absorption measurements is more likely located at about 1 eV below the CB edge, in general agreement with photoelectrochemical measurements. In this sense, the chemistry of oxygen vacancies on  $TiO_2(110)$  can be used to study electron scavenging processes that occur during photocatalysis on TiO<sub>2</sub>.

The EELS spectrum of a thick ice layer on  $TiO_2(110)$  is shown in Figure 2b. All loss features of the underlying  $TiO_2$ -(110) surface are missing because the scattered electrons "see" only the vacuum-ice interface and not the ice- $TiO_2(110)$ interface. Instead, the spectrum reflects the band gap of ice (about 7.5 eV) and the first electronic excitation process of molecular water, namely the  $1b_1 \rightarrow 4a_1$  transition at about 8.3 eV.<sup>67-69</sup>

The EELS spectrum of approximately 1 monolayer of H<sub>2</sub>O on  $TiO_2(110)$  with 14% vacancies is shown in Figure 2c. This water coverage was obtained by preheating a multilayer exposure to 180 K, which desorbed all multilayer water and virtually all second-layer water, leaving only the 270 and 520 K TPD states (see TPD data in Figure 1). As mentioned above, the 270 K TPD state is associated with desorption of water molecularly adsorbed at five-coordinate Ti<sup>4+</sup> sites, whereas the 520 K TPD peak arises from recombinative desorption of OH<sub>br</sub> groups. The EELS spectrum of 1 ML of H<sub>2</sub>O on TiO<sub>2</sub>(110) (Figure 2c) reveals an intense loss feature at 6.2 eV and a weak loss feature at about 8.5 eV. Both of these features are associated with molecularly adsorbed water at five-coordinate Ti<sup>4+</sup> sites because they are absent after heating above 300 K (see Figure 2d). On the basis of the EELS spectrum of ice (Figure 2b), the weak 8.5 eV feature may be assigned to the  $1b_1 \rightarrow 4a_1$  transition in molecularly adsorbed water. Because the  $1b_1 \rightarrow 4a_1$  transition is the lowest energy transition of molecular water and because no transitions relating to gap states were detected in the EELS spectrum of ice (Figure 2b), the loss feature at 6.2 eV for 1 ML of H<sub>2</sub>O probably results from an excitation between water and the oxide. This might correspond to either excitation from the highest occupied molecular orbital of water (1b<sub>1</sub> state) into the oxide's conduction band (CB) or excitation from the oxide's valence band (VB) to the lowest unoccupied molecular orbital of water  $(4a_1)$ . On the basis of published photoemission spectra of monolayer water on  $TiO_2(110)$ , <sup>53,60,70</sup> which provide the location of the 1b<sub>1</sub> orbital relative to the VB edge, the 1b<sub>1</sub>  $\rightarrow$ CB edge transition should be between 7 and 8 eV, which precludes assignment of the 6.2 eV loss to a  $1b_1 \rightarrow CB$ transition. In fact, inverse photoemission results by See et al.<sup>66</sup> indicate that the first maximum in unoccupied Ti 3d states should be at about 1 eV above the CB edge, implying that the maximum loss intensity for a  $1b_1 \rightarrow CB$  transition should be at about 8-9 eV. Assuming that the 8.5 eV loss may be assigned to the water  $1b_1 \rightarrow 4a_1$  molecular transition, then the  $4a_1$  orbital can be placed at about 0.5 to 1.5 eV above the TiO<sub>2</sub> CB edge. A transition from the O 2p-derived maximum density-of-states nearest the VB edge, located at about 5 eV below the VB edge on the basis of photoemission (see references in ref 59), to the  $4a_1$  orbital would give a loss feature at about 6 eV. This transition essentially amounts to the formation of a temporary negative ion state of water (albeit in the vicinity of a hole in the oxide's valence band).

Regardless of the origins of the 6.2 and 8.5 eV losses arising from 1 ML of H<sub>2</sub>O on TiO<sub>2</sub>(110) in Figure 2c, it is important to note that the 0.9 eV loss feature is only slightly attenuated by adsorption of 1 ML of H<sub>2</sub>O at 115 K. This implies that electronic structure of the vacancies is not strongly coupled to electronic states of water or OH<sub>br</sub>. Heating 1 ML of H<sub>2</sub>O on TiO<sub>2</sub>(110) to 370 K desorbs all molecularly adsorbed water (see TPD data of Figure 1), leaving only OH<sub>br</sub> groups from H<sub>2</sub>O dissociation at the vacancies. The EELS spectrum of this surface, shown in Figure 2d, shows that the losses associated with molecularly adsorbed water are absent and that the 0.9 eV loss feature is essentially unchanged from that observed prior to water adsorption (Figure 2a). Recombinative desorption of the OH<sub>br</sub> groups (as water) by heating to 590 K (Figure 2e) also did not significantly change the 0.9 eV loss feature. On the basis of these results, water adsorption and dissociation at vacancies does not "oxidize" the oxygen vacancy-related electronic state that is associated with the 0.9 eV EELS loss, in agreement with previous TPD<sup>48,50,51</sup> and photoemission<sup>60</sup> results. In other words, little or no charge transfer occurs between the vacancy electronic state (Ti<sup>3+</sup>) and the vacancy-bound OH<sub>br</sub>. In contrast, the 0.9 eV loss feature is absent after exposure of the surface to oxygen at temperatures above about 150 K (see Figure 2f for spectrum obtained after O<sub>2</sub> exposure at 700 K). O<sub>2</sub> adsorption below 150 K also results in depletion of the 0.9 eV loss feature; however, a new loss is observed at 2.8 eV associated with an adsorbed O2<sup>-</sup> species.38

3.2. Reaction of O<sub>2</sub> with OH<sub>br</sub> Groups at Oxygen Vacancies on  $TiO_2(110)$ . Surface hydroxyls have been proposed to be involved in electron scavenging processes during photocatalysis over TiO<sub>2</sub>. On the basis of pH dependent changes in photooxidation reaction rates, Poznyak et al.<sup>71</sup> proposed that surface OH groups mediate the photoexcited electron transfer from TiO<sub>2</sub> to chemisorbed O<sub>2</sub>-related species. Liu et al.<sup>10</sup> showed that the amount of HO<sub>2</sub> formed from O<sub>2</sub> scavenging of dyephotosensitized TiO<sub>2</sub> increased and then decreased as the amount of water in a methanol-based suspension was increased. Also, two groups have suggested that electron traps are associated with OH groups. Szczepankiewicz et al.22 proposed that photoexcited electrons were trapped at the surface as Ti<sup>3+</sup>-OH groups, and this trapping was facilitated by the ability of OH groups to dissipate the resulting energy through O-H related vibrations. Similarly, Corrent et al.<sup>72</sup> suggested that changes in the luminescence of trapped electrons brought about by hydration/dehydration indicates that some electron traps are associated with Ti<sup>3+</sup>-OH groups.

In this section we explore the interaction of  $O_2$  with OH groups formed from water dissociation at oxygen vacancy sites. Figure 3 shows H<sub>2</sub>O TPD results from the reaction of  $O_2$  with OH<sub>br</sub> groups on a TiO<sub>2</sub>(110) crystal with 14% oxygen vacancies. In each experiment, a fresh TiO<sub>2</sub>(110) surface was prepared by annealing in UHV at 850 K for 10 min. The TiO<sub>2</sub>(110) surface was then exposed to a multilayer coverage of water and preheated to about 350 K to remove all molecularly adsorbed water leaving only roughly 0.28 ML of OH<sub>br</sub> groups, as shown



**Figure 3.** H<sub>2</sub>O TPD spectra (m/e = 18) obtained after exposure of OH<sub>br</sub> groups (about 0.28 ML) on TiO<sub>2</sub>(110) to various amounts of O<sub>2</sub> at 120 K. The surface with only OH<sub>br</sub> groups (TPD of which is shown in the lower trace) was prepared by preheating a multilayer H<sub>2</sub>O exposure to 370 K and recooling to 120 K prior to O<sub>2</sub> exposure. Spectra are displaced vertically for clarity.

in the "preheated" TPD trace of Figure 1. TPD of 0.28 ML of OH<sub>br</sub> on TiO<sub>2</sub>(110), reproduced from Figure 1, is shown in Figure 3 as the "0 langmuir O<sub>2</sub>" condition. (One langmuir (L) equals an exposure of  $1 \times 10^{-6}$  Torr s.) This surface was regenerated by vacuum annealing prior to each O2 exposure experiment shown in Figure 3. As a function of increasing  $O_2$ exposure (bottom to top in Figure 3), the H<sub>2</sub>O TPD state at 520 K due to recombination of OH<sub>br</sub> groups is progressively "titrated" by reaction with O<sub>2</sub> and replaced by a sharper H<sub>2</sub>O TPD state at about 300-320 K. On the basis of our previous work,<sup>39,49</sup> this new H<sub>2</sub>O TPD peak can be assigned to combination of two terminal OH (OHt) groups adsorbed at nondefect five-coordinate  $Ti^{4+}$  sites that typify the ideal  $TiO_2(110)$  surface. The combination of two OHt groups to form water leaves O adatoms on the surface at the five-coordinate Ti<sup>4+</sup> sites. Oxygen adatoms are also formed from O2 dissociation at oxygen vacancies<sup>38,49</sup> and may be responsible for the "bright spots" observed on the Ti<sup>4+</sup> rows in STM by Diebold and co-workers <sup>73</sup> after exposure of  $TiO_2(110)$  to oxygen at room temperature (RT). The new TPD peak due to OH<sub>t</sub> recombination remained sharp until the O<sub>2</sub> exposure exceeded about 1 L, at which point virtually all OH<sub>br</sub> groups were consumed and a 410 K O<sub>2</sub> state appeared in TPD (see Figure 4) similar to that seen for lowtemperature adsorption of  $O_2$  on the clean surface.  $^{38,39}$  (The broad O<sub>2</sub> feature at about 200 K that increases with exposure is mostly, but not entirely,<sup>39</sup> due to O<sub>2</sub> adsorption on the sample holder, which arises from the fact that O2 was dosed by backfilling. The amount of O2 desorbing in this region is considerably less when O2 is dosed through a directional doser.38) The coincident broadening of the 300-320 K H<sub>2</sub>O TPD peak and the appearance of the 410 K O<sub>2</sub> TPD peak implies that the chemisorbed  $O_2$  perturbed the recombination of  $OH_t$ groups. The 410 K O<sub>2</sub> TPD state arises in Figure 4 from an



**Figure 4.**  $O_2$  TPD spectra (m/e = 32) from the same experiments performed in Figure 3. Note that for simplicity not all of the  $O_2$  TPD data corresponding to each experiment in Figure 3 are shown in Figure 4 (and vice versa).

 $O_2^-$  surface species that is formed by charge transfer from the vacancy-related electronic state to an  $O_2$  molecule adsorbed at cation sites next to (but not at) the vacancy sites.<sup>38</sup> Theoretical calculations by de Lara-Castells and Krause<sup>40,41</sup> predict that very little electron density is required to stabilize  $O_2$  at these sites, leading to the conclusion that the responsible species is better described as a  $O_2^{\delta-}$  species, where  $\delta < 1$ . The possibility that this  $O_2^{\delta-}$  species is responsible for oxidation of the vacancies and reaction with the OH<sub>br</sub> groups will be discussed below.

Figure 3 also shows that a second, considerably broader H<sub>2</sub>O TPD state at 400–420 K results from reaction of O<sub>2</sub> and OH<sub>br</sub>. This state is most apparent in TPD for O<sub>2</sub> exposures above about 0.4 L. Although the identity of the species is not known, it is presumably OH-related and might be from OH<sub>t</sub> groups that have diffused to or formed at step sites. Using STM, Suzuki et al.<sup>74</sup> have recently observed features at step edges on TiO<sub>2</sub>(110) as a result of water exposure at RT that they have proposed to be OH<sub>t</sub> groups. Given that the species responsible for the H<sub>2</sub>O TPD feature at 300–320 K (which we assign to OH<sub>t</sub> groups at nondefect sites) should not be stable on the TiO<sub>2</sub>(110) surface at RT in UHV, the 400–420 K H<sub>2</sub>O TPD feature can tentatively be assigned to a combination of OH<sub>t</sub> groups at step edges. This assignment is consistent with previous TPD results on sputter/ annealed TiO<sub>2</sub>(110).<sup>48</sup>

The TPD data in Figures 3 and 4 were used to estimate the reaction probability of an incident  $O_2$  molecule with an  $OH_{br}$  group on TiO<sub>2</sub>(110). Figure 5 shows the change in the  $OH_{br}$  coverage as a function of  $O_2$  exposure at 120 K. The  $OH_{br}$  coverage was estimated using the H<sub>2</sub>O TPD peak area above 400 K, which tends to overestimate the coverage of the  $OH_{br}$  groups because this lower limit also captures a portion of the 400–420 K H<sub>2</sub>O TPD state. The initial  $OH_{br}$  coverage (in the absence of postdosed  $O_2$ ) was 0.28 ML, or twice the water coverage in the 520 K TPD peak. Figure 5 shows that the  $OH_{br}$ 



**Figure 5.** H<sub>2</sub>O (filled circles, from data in Figure 3) and O<sub>2</sub> (filled triangles, from data in Figure 4) TPD peak area data from the reaction of various amounts of O<sub>2</sub> with 0.28 ML of OH<sub>br</sub> groups on TiO<sub>2</sub>(110). Empty triangles: TPD peak area in the 410 K O<sub>2</sub> TPD peak from O<sub>2</sub> on the clean surface possessing 10% oxygen vacancies (taken from <sup>38</sup>). The dashed lines are drawn to guide the eye.

coverage decreased steeply as a function of O2 exposure during the first 0.4 L of dosed O<sub>2</sub>. Above an O<sub>2</sub> exposure of 0.4 L, the remaining OH coverage was associated with the 400-420 K H<sub>2</sub>O TPD state, and not due to remaining OH<sub>br</sub> groups, as can be seen from the TPD spectra in Figure 3. Using the H<sub>2</sub>O TPD peak area data from O<sub>2</sub> exposures between 0 and 0.4 L, the slope of a least-squares fit indicates that 0.66 OH<sub>br</sub> groups were titrated per incident O<sub>2</sub> molecule in this exposure range. Given that the initial sticking coefficient of O<sub>2</sub> on the clean surface (with vacancies but without OH/H<sub>2</sub>O) at 120 K is about 0.5,<sup>38</sup> these data indicate that the reaction probability of an adsorbed  $O_2$  molecule with an  $OH_{br}$  group on  $TiO_2(110)$  is near unity. As will be shown below, the  $O_2 + OH_{br}$  reaction does not occur at 120 K, and may proceed through an OH<sub>br</sub>-O<sub>2</sub> complex that does not involve a chemisorbed O2 species. The high reaction probability between  $O_2$  and  $OH_{br}$  on  $TiO_2(110)$  is remarkable because it implies that OH<sub>br</sub> groups formed at trapped electron sites on TiO<sub>2</sub> photocatalysts should have a short residence time in the presence of  $O_2$ . It should be noted, however, that the high reaction probability seen from the data of Figure 5 is linked to the O<sub>2</sub> sticking coefficient, which decreases as the adsorption temperature is increased.<sup>38</sup>

Figure 5 also shows the change in the 410 K  $O_2$  TPD peak area as a result of the reaction with OH<sub>br</sub>. On the clean TiO<sub>2</sub>-(110) surface (empty triangles),  $O_2$  adsorbed at low exposures is destined for oxidization of vacancy sites. (These data were taken from a previous study in which the surface vacancy coverage was 10%.<sup>38</sup>) Adsorbed O<sub>2</sub> molecules in excess of the vacancy population (in the clean surface case, occurring for exposures above 0.8 L) are reversibly bound at five-coordinate  $Ti^{4+}$  sites next to the vacancies (along the [110] direction) and evolve in TPD at 410 K. These cation sites are not strictly 4+ but possess some degree of electron density associated with the oxygen vacancies.<sup>40,75–77</sup> The onset of  $O_2$  desorption from  $O_2$ adsorbed in the presence of OH<sub>br</sub> (solid triangles in Figure 5) coincides with the point at which the OH<sub>br</sub> coverage has minimized (circles), and is consistent with that observed on the clean surface, with the noted consideration that the vacancy populations were different in the two sets of experiments (10% for the clean surface<sup>38</sup> and 14% in this study). Assuming that the O<sub>2</sub> sticking probabilities at 120 K are similar in the two cases (O2 on the surface with and without vacancies filled with



**Figure 6.**  $H_2^{16}O(m/e = 18$ , solid traces) and  $H_2^{18}O(m/e = 20$ , dashed traces) TPD spectra obtained after reaction of 0.08 L O<sub>2</sub> with 0.28 ML of <sup>16</sup>OH<sub>br</sub> groups on TiO<sub>2</sub>(110). Lower traces are TPD in the absence of O<sub>2</sub> exposure, whereas the middle and upper traces are TPD spectra obtained after exposure of <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub>, respectively. The upper and middle spectra are displaced vertically for clarity.

 $OH_{br}$  groups) and taking into account the different vacancy populations of the two samples, the similar onsets for  $O_2$  TPD uptakes imply that roughly the same amount of  $O_2$  is consumed per vacancy in the low exposure regime for the two cases. In other words, just as one  $O_2$  molecule is consumed per vacancy on the clean surface,<sup>38</sup> it appears that one  $O_2$  is consumed per vacancy when the vacancies are filled with dissociated water molecules. Because all of the  $OH_{br}$  groups are consumed, the ratio of  $O_2$  consumed per  $OH_{br}$  group is 1:2.

Additional insights into the reaction of O2 with OHbr groups were obtained using isotopic labeling studies. Figure 6 shows H<sub>2</sub><sup>16</sup>O and H<sub>2</sub><sup>18</sup>O TPD traces for <sup>16</sup>OH<sub>br</sub> groups alone (bottom), after exposure of 0.08 L  ${}^{16}O_2$  to  ${}^{16}OH_{br}$  groups (middle), and after exposure of 0.08 L  $^{18}O_2$  to  $^{16}OH_{br}$  groups (top). In each case, the clean surface oxygen vacancy population was 14%. In these experiments, <sup>18</sup>O<sub>2</sub> was dosed by backfilling the chamber, and as a result the walls of the mass spectrometer ionizer region were unavoidably incorporated with <sup>18</sup>O, resulting in small amounts of spurious <sup>16</sup>O-<sup>18</sup>O scrambling in subsequent water TPD experiments (see bottom and middle sets of traces). A similar effect occurred in the opposite direction with desorption of H<sub>2</sub><sup>18</sup>O registering H<sub>2</sub><sup>16</sup>O signal due to oxygen scrambling with <sup>16</sup>O on the walls of the mass spectrometer. (The origin of this problem was easily diagnosed by observing the <sup>16</sup>O:<sup>18</sup>O ratio in the desorption of multilayer water.<sup>49</sup>) Despite this experimental artifact, it is clear that the reaction of  ${}^{18}O_2$  with <sup>16</sup>OH<sub>br</sub> groups results a significant portion of the 300 K water TPD peak containing <sup>18</sup>O, but virtually none of the unreacted OH<sub>br</sub> groups that recombinatively desorb at 520 K being incorporated with <sup>18</sup>O (top set of Figure 6). This result indicates that <sup>18</sup>O<sub>2</sub> does not displace <sup>16</sup>OH<sub>br</sub> groups from vacancies onto five-coordinate Ti<sup>4+</sup> sites, but that <sup>18</sup>O<sub>2</sub> abstracts hydrogen from the <sup>16</sup>OH<sub>br</sub> groups to form an unknown surface intermediate that



**Figure 7.** Fourier deconvoluted HREELS spectra from the reaction of  $O_2$  with  $OH_{br}$  groups on TiO<sub>2</sub>(110) possessing 14% oxygen vacancy sites. The traces labeled (a) are for about 1.2 ML of H<sub>2</sub>O adsorbed at 120 K. Trace (b) is from the surface in (a) preheated to 375 K, which isolates only the  $OH_{br}$  groups on the surface. Trace (c) is from exposure of the surface in (b) to 2 L O<sub>2</sub> at 120 K. Trace (d) is from the surface in (c) preheated to 230 K. Trace (e), in contrast, is from a switch in the order of  $O_2/H_2O$  adsorption, in which approximately 1 ML of H<sub>2</sub>O is adsorbed after oxygen vacancy sites were first filled by exposure to 4 L O<sub>2</sub> at 120 K (with a preheating step to 575 K to desorb molecularly adsorbed O<sub>2</sub>). Spectra were recorded at 120 K, and are displaced vertically for clarity.

eventually decomposes to <sup>18</sup>OH<sub>t</sub> groups. On the basis of studies on TiO<sub>2</sub> photocatalysts,<sup>1,10–12,14,35</sup> it seems likely that this intermediate is a HO<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> species. It should also be noted that at higher <sup>18</sup>O<sub>2</sub> exposures (above 1 L), only <sup>18</sup>O<sub>2</sub> was observed in the 410 K TPD peak (no <sup>16</sup>O<sub>2</sub> or <sup>16</sup>O<sup>18</sup>O). This indicates that the 410 K O<sub>2</sub> TPD peak is due to molecularly adsorbed O<sub>2</sub>, and not recombinative O<sub>2</sub> desorption, in agreement with results from the clean surface.<sup>38</sup> The origin of <sup>18</sup>O<sub>2</sub> exchange with polycrystalline TiO<sub>2</sub> surfaces during UV exposure, observed for example by Courbon et al.<sup>78,79</sup> and by Sato<sup>80</sup> to yield <sup>16</sup>O<sup>18</sup>O and <sup>16</sup>O<sub>2</sub>, may not be linked to chemistry occurring on (110) terminations or may not be observable in UHV on TiO<sub>2</sub>(110) because of a "pressure gap".

HREELS analysis also provides insights into the reaction of O<sub>2</sub> and OH<sub>br</sub> on TiO<sub>2</sub>(110). Figure 7 shows Fourier deconvoluted HREELS<sup>81</sup> spectra for various combinations of H<sub>2</sub>O and O<sub>2</sub> on a TiO<sub>2</sub>(110) surface possessing about 14% oxygen vacancies. The traces shown in Figure 7a correspond to the deconvoluted spectra for 1.2 ML of H<sub>2</sub>O. The 1.2 ML of H<sub>2</sub>O surface was prepared by adsorption of a thick H<sub>2</sub>O multilayer followed by heating to 180 K, which desorbed all the multilayer and most of the second-layer water.<sup>52</sup> The presence of some second-layer water is evidenced by the broad  $\nu$ (OH) feature centered at 3250 cm<sup>-1</sup>, whereas the more intense feature at 3500 cm<sup>-1</sup> is due to molecularly adsorbed water in the monolayer.<sup>52</sup> (Note that there is intensity in the loss region of each spectrum in Figure 7a–f

at about 2200  $\text{cm}^{-1}$ . This may be due to an artifact of the deconvolution process or it may result from background CO adsorption.)

Two significant differences are present in the HREELS spectrum of water on TiO<sub>2</sub>(110) with 14% vacancies (Figure 7a) versus what was reported earlier for water on the nearly defect-free TiO<sub>2</sub>(110) surface.<sup>52</sup> The first difference is that the "phonon remnants" (the intensity leftover in the first multiple loss features at 1205 and 1520 cm<sup>-1</sup> after Fourier deconvolution) are considerably more intense than what was observed on the nearly defect-free TiO<sub>2</sub>(110) surface. In this case, the  $\delta$ (HOH) mode of water, marked with an asterisk in the "x100" spectrum of Figure 7a, is barely discernible from the 1520 cm<sup>-1</sup> phonon remnant, whereas the  $\delta$ (HOH) loss was more intense than the phonon remnant on the nearly defect-free surface.52 This comparison suggests that the intensity in the multiple phonon remnant increases as the surface oxygen vacancy population increases. Wulser and Langell<sup>82</sup> have proposed that the intensity left in the first set of multiple phonons after Fourier deconvolution results from non-Poisson behavior in the scattering of electrons from oxides, likely as a result of combinations of impact and dipole excitation events. In this case, the probability of exciting a phonon by impact scattering increases as the population of surface electronic defects increases. The second difference between the HREELS spectrum in Figure 7a and that observed earlier on nearly defect-free  $TiO_2(110)^{52}$  is the presence of a more intense 3665 cm<sup>-1</sup> loss in the present case. As it turns out, this difference is also linked to the presence of a much higher population of oxygen vacancy defects in the present case (about 14%) versus the trace level present in the earlier study. Recently, Brookes and co-workers<sup>53</sup> reassigned the small 3690 cm<sup>-1</sup> loss observed in the previously published HREELS spectra by the present lead author<sup>52</sup> to OH<sub>br</sub> groups from water dissociation at oxygen vacancies on the basis of their STM results (as opposed to the previously proposed assignment of OH groups at steps). Given the intensity of the 3665 cm<sup>-1</sup> loss in Figure 7a, we concur with the reassignment of this loss by Brookes and co-workers. Inspection of the relative  $\nu(OH)$ intensities for molecularly adsorbed water (at 3500 cm<sup>-1</sup>) and for OH<sub>br</sub> (at 3665 cm<sup>-1</sup>) indicates that the excitation probability of the latter is roughly twice that of the former on the basis of the relative coverages of the two species. This may indicate that the O-H bond direction in the OH<sub>br</sub> groups is oriented normal of the surface, whereas the O-H bond directions of molecularly adsorbed water are inclined from the surface normal.

The presence of the  $\nu$ (OH) loss at 3665 cm<sup>-1</sup> due to OH<sub>br</sub> groups in Figure 7a suggests that water dissociates at oxygen vacancies at or below 180 K (the preheating temperature used to desorb multilayer water—see above). This is consistent with the STM results of Schaub et al.<sup>54</sup> who also observed water dissociation at vacancies on TiO<sub>2</sub>(110) at 180 K. In contrast, Brookes et al.<sup>53</sup> proposed that water did not dissociate at vacancies until 290 K on the basis of the temperature at which OH features became apparent in their VB photoemission spectra.

The HREELS spectrum in Figure 7b shows that all molecularly adsorbed water is desorbed after heating the surface to 375 K, leaving only the 3665 cm<sup>-1</sup> loss associated with the OH<sub>br</sub> groups. Exposure of these OH<sub>br</sub> groups to 2 L O<sub>2</sub> at 120 K did not remove the 3665 cm<sup>-1</sup> loss (Figure 7c), although it broadened the loss feature somewhat. This suggests that O<sub>2</sub> and OH<sub>br</sub> groups interact sufficiently at 120 K to affect the latter's  $\nu$ (OH) mode, but that a reaction does not take place. This behavior is consistent with previous observations that at low-temperature O<sub>2</sub> is adsorbed weakly to the surface, possibly in a



**Figure 8.** EELS spectra from the interaction of water and oxygen on  $TiO_2(110)$  with 10% oxygen vacancy sites. The solid line trace corresponds to the surface after annealing at 850 K. The dashed line trace is after decomposition of water in the oxygen vacancies, which generates about 0.2 ML of  $OH_{br}$  groups. The dotted line trace corresponds to the spectrum obtained after reaction of the 0.2 ML of  $OH_{br}$  groups with  $O_2$  at 90 K. Spectra were recorded in the specular direction at 90 K with an electron beam energy of 25 eV.

physisorbed state.<sup>38,39</sup> Heating the surface of Figure 7c to 230 K resulted in almost complete attenuation of the 3665 cm<sup>-1</sup> loss (see Figure 7d), indicating that almost all of the OH<sub>br</sub> groups were removed. The product of the reaction of  $O_2$  and  $OH_{br}$ , however, is not evident in HREELS. As shown in Figure 7d, the  $\nu$ (OH) region (3200–3800 cm<sup>-1</sup>) is essentially devoid of loss features despite the fact that TPD clearly shows that no water has desorbed below 230 K (see top TPD trace of Figure 3). The absence of a  $\nu$ (OH) loss at 3500 cm<sup>-1</sup> indicates that the reaction of O<sub>2</sub> and OH<sub>br</sub> does not generate molecularly adsorbed water. We therefore propose that the reaction product of O2 and OHbr at 230 K possesses O-H bonds that are significantly inclined parallel to the surface so as to render them with little or no dynamic dipole moment normal to the surface (a necessity for dipole scattering in HREELS). Such a condition may arise from hydrogen-bonding interactions, for example, between neighboring OH<sub>t</sub> groups at five-coordinate Ti<sup>4+</sup> sites. Alternatively, an intermediate species such as HO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> may be formed which then decomposes to OH<sub>t</sub> groups.

Finally, Figure 7e provides additional support for the 3665 cm<sup>-1</sup> loss being due to  $OH_{br}$  groups. In this HREELS spectrum, the TiO<sub>2</sub>(110) surface was pretreated with 4 L O<sub>2</sub> at 120 K, followed by heating to 535 K *prior to* water exposure at 120 K. The O<sub>2</sub> adsorption and preheating treatments resulted in all oxygen vacancies being oxidized.<sup>38,49</sup> The HREELS spectrum of 1 ML of H<sub>2</sub>O on this surface (Figure 7e) shows the presence of molecularly adsorbed water at 3500 cm<sup>-1</sup>, but no sign of loss intensity at 3665 cm<sup>-1</sup> from OH<sub>br</sub> groups, consistent with the absence of oxygen vacancies.

The reaction between  $O_2$  and  $OH_{br}$  was also evident in EELS. Figure 8 shows EELS spectra collected from a TiO<sub>2</sub>(110) crystal





**Figure 9.** Proposed model for the reaction of  $O_2$  with  $OH_{br}$  groups on  $TiO_2(110)$ . The upper drawing represents a view of the surface with an oxygen vacancy site in the middle the row of bridging O sites. The middle drawing illustrates the dissociation of water in the vacancy to form to  $OH_{br}$  groups. The lower drawing illustrates the end point in the reaction between  $O_2$  and  $OH_{br}$ , wherein the vacancy is filled and two  $OH_t$  groups are formed at adjacent five-coordinate  $Ti^{4+}$  sites.

that possessed about 10% oxygen vacancy sites. The EELS spectrum for the clean surface with 10% oxygen vacancies exhibits an intense loss at 0.82 eV due to oxygen vacancies. As was the case of the crystal with 14% oxygen vacancies (see Figure 2), exposure of this surface to water (followed by desorption of all molecular water by heating to 380 K) did not significantly deplete the vacancy-related loss feature (dashed line trace in Figure 8). Subsequent exposure to O<sub>2</sub> (of an unknown exposure) at 90 K (dotted line trace in Figure 8) resulted in a nearly complete attenuation of the vacancy loss feature. Heating the surface to 230 K and above (data not shown) did not change the EELS spectrum. In contrast to the vibrational data shown in Figure 7, the electronic spectra presented in Figure 8 suggests that the charge-transfer process between O<sub>2</sub> and OH-filled vacancies takes place at 90 K.

The results in Figure 8 provide evidence that the reaction of O2 with OHbr is accompanied by the equivalent of electron scavenging of the trapped electrons at the Ti<sup>3+</sup>-OH<sub>br</sub> sites. Figure 9 presents a tentative model for the reaction of O<sub>2</sub> with  $OH_{br}$  groups on TiO<sub>2</sub>(110). The top model shows a space-filling representation of the  $TiO_2(110)$  surface with a single oxygen vacancy site. Both cations at the vacancy can be thought of as being Ti<sup>3+</sup> in nature, although it is becoming more apparent that these electrons are spin polarized and possess some degree of delocalization to adjacent Ti<sup>4+</sup> cations.<sup>40,75-77</sup> Adsorption and dissociation of water at the oxygen vacancy results in two equivalent OH<sub>br</sub> groups, as shown in the middle model of Figure 9. As described above, this process does not oxidize the Ti<sup>3+</sup> cations at the vacancy. However, because the two OH<sub>br</sub> groups are, in principle, indistinguishable from each other, the electrons associated with the original Ti<sup>3+</sup> cations should be delocalized over both OH<sub>br</sub> sites, yielding the equivalent of one electron per OH<sub>br</sub> group. Previous results show that the hydrogen atoms

readily diffuse along the rows of bridging oxygen anions during heating and recombine to abstract water and form new oxygen vacancies randomly located along the bridging oxygen rows.<sup>48</sup> This implies that either the hydrogen atoms diffuse along the rows of bridging oxygen sites as H radicals or as protons with the electron passed from underlying cation to cation as the proton is transferred along the row of bridging O<sup>2-</sup> sites. It is unclear whether the hydrogen atoms diffuse independently or as pairs, although two recent STM<sup>53,54</sup> studies show no evidence for pairing of the bright spots associated with OH<sub>br</sub> groups. Irrespective of this point, the lower model of Figure 9 conceptually illustrates the conversion of OH<sub>br</sub> groups to OH<sub>t</sub> groups as a result of reaction with O<sub>2</sub>. The model emphasizes three points from the data: (1) that the oxygen vacancies are "oxidized", that is, the sites are filled with bridging  $O^{2-}$  sites, (2) that each reacted  $O_2$  molecule consumes two  $OH_{br}$  groups, and (3) that the resulting O-H bonds in the products (presumably OH<sub>t</sub> groups and/or HO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> intermediates) are tilted from the surface normal. After desorption of water in the 300-320 K TPD peak (Figure 3) the surface then possesses a coverage of oxygen adatoms located at five-coordinate Ti<sup>4+</sup> sites equivalent to the original oxygen vacancy population. These species are not detected in photoemission or in EELS, but their presence on the surface is evident in the chemistry of coadsorbates. We have previously studied the reaction of these oxygen adatoms species with coadsorbed water,<sup>49</sup> ammonia<sup>49</sup> and methanol,<sup>83</sup> and have shown that they abstract protons from the O-H and N-H bonds of neighboring coadsorbates. In the case of water, this reactions yields two OHt groups. Therefore, the final product from the interaction of O<sub>2</sub> with vacancies on the clean surface is the same as that from O2 reacting with OHbr groups formed by dissociation of water at vacancies, that being filled vacancies and deposited oxygen adatoms.

These results provide evidence for one mechanism by which  $O_2$  scavenges trapped electrons on  $TiO_2$  photocatalysts. The overall stoichiometry for the scavenging of electrons by reaction of  $O_2$  with  $OH_{br}$  groups formed at oxygen vacancies sites is illustrated in the following reactions:

where "vac" and " $O_{br}^{2-}$ " correspond to oxygen vacancy and bridging  $O^{2-}$  anion sites, respectively, and the  $OH_t$  and  $O_a$ species are located at nondefect five-coordinate  $Ti^{4+}$  sites. (The temperature references are the points at which each of these processes is observed.) Two electrons are localized at each vacancy on the clean surface, and thus one per  $OH_{br}$  group after dissociation of water at the vacancies. On the basis of these charge counting arguments, the  $OH_t$  and  $O_a$  species are charge neutral as, for example, water would be if adsorbed at the same sites. Although the resulting  $OH_t$  groups are presumably less thermodynamically stable than the  $OH_{br}$  groups (on the basis of their respective recombinative desorption temperatures), the thermodynamic basis for the conversion of  $OH_{br}$  groups to  $OH_t$ groups arises from the greater stability of a  $O^{2-}_{br}$  site than that of  $OH_{br}$ . The overall stoichiometry for this chemistry is

$$\operatorname{vac}(2e^{-}) + O_2(g) \rightarrow O_{br}^{2-} + O_a$$

which, as mentioned above, is the same as that observed for the oxidation of oxygen vacancies on the clean surface by  $O_2$ .<sup>38,49</sup>



**Figure 10.** (A)  $D_2O$  TPD spectra (m/e = 20) from varying precoverages of  $D_2O$  on a TiO<sub>2</sub>(110) surface possessing 2.5% oxygen vacancies in each case followed by a 10 L O<sub>2</sub> exposure at 90 K. The lower portion of (A) is for submonolayer precoverages of  $D_2O$ , whereas the upper portion is for precoverages above 1 ML. The inset to (A) shows the temperature region between 450 and 550 K for one TPD spectrum from each case. (B) O<sub>2</sub> TPD spectra (m/e = 32) from the precoverages of D<sub>2</sub>O in the submonolayer regime shown in (A). Spectra are displaced vertically for clarity.

3.3. Blocking of the  $O_2 + OH_{br}$  Reaction by Preadsorbed Water. Numerous groups have observed that water has both a positive and negative effect on photochemical rates at the gaseous-TiO<sub>2</sub> heterogeneous interface. Fu et al.,<sup>16</sup> who recently reviewed the literature on this subject, pointed out that photooxidation rates are generally higher in the gas phase compared to the aqueous phase due in large part to the role of water. For example, the rates for photooxidation of many gas-phase species over TiO<sub>2</sub> have been observed to increase as the relative humidity (RH) is increased from 0% to about 30-60% but then decrease as the RH is increased to saturation.84-94 The increase rates are typically interpreted in terms of hole-related processes, although some groups have found that water impacts how photoexcited electrons are scavenged by O2.10,22,71,72,95 By and large, the inhibition effect of high RH has been ascribed to competition for adsorption sites between water and the reactant being photooxidized.

In this section we examine how coadsorbed water influences the reaction of O<sub>2</sub> with bridging hydroxyl groups (in this case, OD<sub>br</sub> groups) formed from water (D<sub>2</sub>O) decomposition at oxygen vacancies on TiO<sub>2</sub>(110). Figure 10 shows D<sub>2</sub>O (A) and  $O_2$  (B) TPD spectra from the reaction of  $O_2$  with  $OD_{br}$  as a function of increasing preadsorbed D<sub>2</sub>O coverage on a TiO<sub>2</sub>-(110) crystal possessing 2.5% oxygen vacancy sites. In these experiments, D<sub>2</sub>O was adsorbed at 90 K at coverages in case excess of that needed to form the  $OD_{br}$  groups. The excess  $D_2O$ was not removed from the surface before O<sub>2</sub> exposure, as was the case in the experiments discussed in the previous section. A near saturation O<sub>2</sub> exposure of 10 L at 90 K was used. Any influence of coadsorbed water on the reaction of O2 with ODbr groups should be evident by changes in the D<sub>2</sub>O TPD spectrum. Starting with the bottom portion of the D<sub>2</sub>O panel (A), one can see that the D<sub>2</sub>O TPD traces possess similar trailing edge profiles for D<sub>2</sub>O precoverages between 0.20 and 0.90 ML, with an increasing D<sub>2</sub>O peak area that shifts to lower temperature with increasing coverage. Oxygen vacancies are filled with OD<sub>br</sub> groups for all of these precoverages of D<sub>2</sub>O, yielding in each case an OD<sub>br</sub> coverage of about 0.05 ML. The coincidence of



**Figure 11.**  $D_2O$  (hollow triangles) and  $O_2$  (filled circles) TPD peak area data taken from the spectra in Figure 10. Only the  $D_2O$  TPD peak area above 400 K was used to approximate the  $OD_{br}$  coverage, and the  $O_2$  TPD peak area is from the 410 K  $O_2$  TPD peak.

the trailing edges of all the D<sub>2</sub>O TPD traces (located above 300 K) indicates that the extent of the  $O_2 + OD_{br}$  reaction was not influenced by submonolayer coverages of D<sub>2</sub>O. Consistent with this observation, the 500 K D<sub>2</sub>O TPD peak from recombination of OD<sub>br</sub> groups was absent for D<sub>2</sub>O precoverages in the submonolayer regime (see the inset of Figure 10A), indicating complete conversion of OD<sub>br</sub> to OD<sub>t</sub>. The corresponding O<sub>2</sub> TPD spectra as a function of D<sub>2</sub>O precoverage (Figure 10B) reveal that preadsorbed D<sub>2</sub>O blocked O<sub>2</sub> adsorption sites associated with 410 K O<sub>2</sub> TPD state to the extent that no O<sub>2</sub> TPD signal was detected after preadsorption of 0.8 ML of D<sub>2</sub>O. This effect is better illustrated in Figure 11 using the peak area from the 410 K O<sub>2</sub> TPD state as a function of the D<sub>2</sub>O precoverage. The O2 TPD peak area (circles) linearly decreased for increasing D<sub>2</sub>O precoverages up to 0.6 ML and then more abruptly attenuated to zero by the 0.8 mL of D<sub>2</sub>O precoverage. However, the TPD peak area in the 500 K D<sub>2</sub>O state (triangles), which reflects the OD<sub>br</sub> coverage, was near zero and did not

increase, indicating that the extent of  $O_2 + OD_{br}$  reaction was not influenced by  $D_2O$  precoverage in submonolayer regime.

In contrast to the absence of an effect for submonolayer precoverages of D<sub>2</sub>O, data in the upper panel of Figure 10A show that D<sub>2</sub>O precoverages in excess of 1 ML had a significant effect on the  $O_2 + OD_{br}$  reaction. The trailing edge of the 270 K D<sub>2</sub>O TPD peak shifted toward lower temperature as the precoverage of D<sub>2</sub>O was increased above 1 ML to the extent that the TPD spectra of 1.5 ML of D<sub>2</sub>O with and without subsequent O<sub>2</sub> exposure were nearly identical. Coincident with the change in the trailing edge of the 270 K D<sub>2</sub>O TPD peak, the inset of Figure 10A shows that the D<sub>2</sub>O TPD state due to  $OD_{br}$  recombination reappeared as the  $D_2O$  precoverage is increased above the 1 ML point (see also the TPD peak area data in Figure 11). In the D<sub>2</sub>O precoverage range between 1 and 1.5 ML, the first layer has filled with D<sub>2</sub>O and second layer with D<sub>2</sub>O (175 K TPD peak) begins to fill. Second-layer water is adsorbed to the surface through hydrogen-bonding interactions with the rows of bridging oxygen sites.<sup>51,52</sup>

Several observations can be gleaned from the data in Figures 10 and 11. First, preadsorbed water does not exhibit a strong preference for five-coordinate cation sites in the vicinity of OH<sub>br</sub>/ OD<sub>br</sub> groups (the adsorption sites of O<sub>2</sub> in the 410 K TPD peak<sup>38</sup>) over similar sites far from these groups. If this were the case, preadsorption of 0.1 ML of D<sub>2</sub>O would have completely blocked all O<sub>2</sub> adsorption into the 410 K TPD state, which was not observed. Second, when preadsorbed water molecules occupy O<sub>2</sub> adsorption sites, subsequent exposure to O<sub>2</sub> does not displace these water molecules. This is evident from the fact that the O<sub>2</sub> TPD peak area progressively decreased as a function of D<sub>2</sub>O precoverage as opposed to staying nearly constant at low D<sub>2</sub>O precoverages. Finally, and perhaps of greater importance, the data in Figures 10 and 11 indicate that the reaction of O<sub>2</sub> and OD<sub>br</sub> likely involves a direct O<sub>2</sub>-OD<sub>br</sub> interaction that does not involve the chemisorbed O2 state associated with the 410 K O2 TPD state. Although first-layer water had no effect on the  $O_2 + OD_{br}$  reaction, second-layer water prevented O<sub>2</sub> from reacting with OD<sub>br</sub> groups. The immediate product of the reaction (DO<sub>2</sub> and/or D<sub>2</sub>O<sub>2</sub>) may displace monolayer water or adsorb at cation sites after water desorption.

The interaction between a second-layer water molecule and a  $OH_{br}/OD_{br}$  group should be somewhat different from that of the interaction of a second-layer water molecule with a  $O^{2-}_{br}$  site because  $OD_{br}$  groups should function primarily as hydrogenbond donors whereas  $O^{2-}_{br}$  sites can only function as hydrogenbond acceptors. However, the fact that the extent of the reaction decreases progressively for  $D_2O$  precoverages between 1 and 1.5 ML indicates that second-layer  $D_2O$  has a weak preference for adsorption at  $OD_{br}$  versus  $O^{2-}_{br}$  sites.

The role that second-layer water plays in blocking the reaction between  $O_2$  and  $OD_{br}$  groups at electronic defects on  $TiO_2$  surfaces is schematically shown in Figure 12. In the absence of second-layer water (left side of Figure 12), incident  $O_2$  molecules react with  $OH_{br}/OD_{br}$  groups to form (ultimately)  $OH_{t}/OD_t$  groups and to oxidize the electronic defects ("trapped" electrons) associated with the original oxygen vacancy sites. In contrast, an overlayer of water blocks access of  $O_2$  to these  $OH_{br}/OD_{br}$  groups (right side of Figure 12), presumably by hydrogenbonding to the  $OH_{br}/OD_{br}$  groups, thus preventing charge transfer to  $O_2$  and conversion of  $OH_{br}/OD_{br}$  groups to  $OH_t/OD_t$  groups.





into OH, groups

**Figure 12.** Schematic model illustrating the effect of second-layer water on the reaction of  $O_2$  with  $OH_{br}$  groups on  $TiO_2(110)$ .

# 4. Implications for Electron Scavenging Processes on $\ensuremath{\text{Ti}O_2}$

The reaction of O<sub>2</sub> with OH<sub>br</sub> groups formed from water dissociation at electronic defects on  $TiO_2(110)$  is similar in two ways to proposed mechanisms in which O<sub>2</sub> scavenges trapped electrons during heterogeneous photocatalysis over TiO<sub>2</sub>. First, in both cases surface Ti<sup>3+</sup>-OH sites are oxidized by O<sub>2</sub>. In heterogeneous photochemical studies, several groups have proposed these sites are formed from electron trapping at Ti<sup>4+</sup>-OH groups,<sup>10,22,71,72,95</sup> whereas on TiO<sub>2</sub>(110) they result from water dissociation at oxygen vacancies. Nevertheless, the resulting surface species in both cases are similar. In the UHV experiments, the species formed from the reaction of  $O_2 + OH_{br}$ involves hydrogen atom transfer to a physisorbed O<sub>2</sub> molecule and formation of an unidentified intermediate species (presumably  $HO_2/H_2O_2$ ) which eventually decomposes to form  $OH_t$ groups. Second, results in this study showing that second-layer water blocks the reaction of O2 and OHbr are consistent with the inhibiting influence of water on the rates of photooxidation at the gas-TiO<sub>2</sub> interface,  $^{84-94}$  as well as the  $^{18}O_2 - ^{16}O_2$ exchange process observed by Sato<sup>80</sup> during UV illumination of TiO<sub>2</sub>. These studies show that photooxidation rates increase with increasing RH from 0 to 30-60%, but then decrease as the RH is increased to saturation. The increased rates in the low RH range have typically been ascribed to enhanced rates of OH radical production arising from hole-related processes, whereas overall rate degradation at higher RH levels has been ascribed to blocking of reactant adsorption sites. Results in this study open the possibility that second-layer water (which should be more prevalent at high RH) inhibits the ability of O<sub>2</sub> to scavenge trapped electrons from TiO<sub>2</sub> photocatalysts via reaction with Ti<sup>3+</sup>-OH groups. Similar arguments have been applied to the influence of water on the extent of photon-induced adsorption of O2 on TiO2.96-100

Finally, one might ask, if a second layer of water blocks access of  $O_2$  to sites where electron scavenging can take place then how is it that photooxidation can take place in solution or at high RH? The answer to this question comes from considering the dynamics of the two systems discussed here (UHV versus solution/high RH). The UHV experiments in which second-layer water is observed to block the  $O_2 + OH_{br}$  reaction (see Figure 10) are similar to those of the solution and high RH cases in that the "coverage" of second-layer water is near saturation.

However, in the UHV experiments the rates of adsorption and desorption of water from the second layer are zero below 170 K, whereas the adsorption/desorption rates of water associated with what could be termed the "second layer" in solution or at high RH are nonzero and more-or-less in equilibrium with each other. Therefore, the UHV situation provides a static "snapshot" of the dynamic situation taking place in solution or at high RH. In the latter,  $O_2$  can find its way to electron trap states on the surface because the second-layer water molecules are adsorbing and desorbing, which provides  $O_2$  and other species partial access to the surface. Therefore, the electron scavenging reaction does occur in solution and at high RH, although many attempts by impinging O<sub>2</sub> molecules are "turned away" from the surface when they encounter water hydrogen-bonded to the OH groups located at electron trap sites. This behavior, which is difficult to detect in solution, is revealed by the "static" UHV experiments performed here.

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