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# Reactions of fluid and lattice oxygen mediated by interstitial atoms at the TiO<sub>2</sub>(110)–water interface†

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O<sub>2</sub> interacts with TiO<sub>2</sub> surfaces in numerous aqueous reactions for clean hydrogen production, wastewater cleanup, reduction of CO<sub>2</sub> and N<sub>2</sub>, and O<sub>2</sub> sensing. In many cases, these reactions involve reversible exchange of O with the solid, whose participation is usually thought to require oxygen vacancies (V<sub>O</sub>). Based on measurements of oxygen isotopic self-diffusion in rutile TiO<sub>2</sub> under water, this work proposes a different perspective centered on O interstitial atoms (O<sub>i</sub>). Experiments with varying concentrations of O<sub>2</sub> and mole fractions of <sup>18</sup>O show that the (110) surface facilitates O exchange with both the H<sub>2</sub>O liquid and its dissolved O<sub>2</sub>. First-principles calculations indicate that on-top and “surface O<sub>i</sub>” configurations of adsorbed O participate sequentially in the exchange process. Adsorbed OH appears to provide a single pathway for H<sub>2</sub>O and O<sub>2</sub> to contribute oxygen, although fitting the diffusion data to simple models indicates that H<sub>2</sub>O contributes more. Because rutile TiO<sub>2</sub> is a prototypical metal oxide, this picture based on O<sub>i</sub> probably generalizes in many cases to other oxides – explaining important aspects of their thermal, electrochemical, and photochemical reactions with dissolved O<sub>2</sub>.

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## 1. Introduction

O<sub>2</sub> interacts with water-submerged TiO<sub>2</sub> surfaces in many aqueous reactions for production of clean hydrogen,<sup>1–5</sup> cleanup of wastewater,<sup>6–11</sup> reduction of N<sub>2</sub> to NH<sub>3</sub>,<sup>12–16</sup> reduction of CO<sub>2</sub> to hydrocarbons,<sup>17,18</sup> production of H<sub>2</sub>O<sub>2</sub>,<sup>19</sup> and sensing of O<sub>2</sub>.<sup>20</sup> For the oxygen evolution reaction (OER) by photocatalysis<sup>21,22</sup> and electrocatalysis,<sup>23</sup> significant attention focuses on participation of lattice oxygen from TiO<sub>2</sub>. This attention extends to other metal oxides<sup>24–28</sup> for the OER, the oxygen reduction reaction<sup>29–31</sup> (ORR) and advanced oxidation processes (AOP).<sup>11</sup> Many authors use the term “lattice oxygen

mechanism” (LOM) to describe the chemical pathways for exchange of atoms between O<sub>2</sub> and the solid,<sup>21–23,25–27,32,33</sup> although “Mars–van Krevelen mechanism” prevails among other authors.<sup>31,34</sup> Such mechanisms contrast with pathways involving atoms derived only from the liquid, termed an “adsorbate evolution mechanism” in the OER.<sup>10,26,35</sup>

Regardless of the oxide or driving force (thermal, electrochemical, or photochemical), O vacancies (V<sub>O</sub>) are usually thought to mediate participation of lattice oxygen.<sup>25,27,33,35</sup> However, this physical picture has been questioned recently,<sup>29</sup> partly because O interstitial atoms (O<sub>i</sub>) appear to facilitate lattice O participation in some cases.<sup>29,30</sup> This literature struggles to reconcile the notion of “active oxygen” in the lattice with the assumed need for surface V<sub>O</sub> to assist the reaction. Furthermore, mediation by vacancies contains implicit inconsistencies. For example, the OER on TiO<sub>2</sub> and perovskites often operates under intensely oxidizing conditions<sup>26,35</sup> (strongly alkaline pH, high applied potential, and high O<sub>2</sub> concentration) that are not hospitable for surface V<sub>O</sub>, which reflect chemical reduction. Moreover, increasing the V<sub>O</sub> concentration in O-deficient perovskites increases the barrier for participation of lattice O.<sup>26</sup> In other words, the reaction seems to require vacancies, yet increasing their concentration diminishes the rate (*e.g.*, in SrCoO<sub>3</sub><sup>36</sup>).

As described elsewhere,<sup>29,30</sup> an alternate perspective based on O<sub>i</sub> merits consideration in many cases. Under O-rich

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† Electronic supplementary information (ESI) available: Method for determination of profile metrics; statistical analysis example calculation; adsorption models (linear and dual pathway); table of surface coverages of <sup>18</sup>O and <sup>16</sup>O; additional supplementary figures and tables including change in pH vs. ln(*F*<sub>18</sub>), profile metrics vs. applied potential *V*<sub>appl</sub>, *F*-tests for null hypothesis on slopes of profile metrics vs. *V*<sub>appl</sub>, histograms of the five profile metrics at 70 °C with and without applied bias, atomic geometries of TiO<sub>2</sub>(110) with and without adsorbed bridging hydroxyls, adsorption energy and Bader charge of adsorbed O on TiO<sub>2</sub>(110) under Ti-rich conditions. See DOI: <https://doi.org/10.1039/d5cp00319a>



conditions,  $O_i$  mediates O exchange between several different binary oxides and liquid  $H_2O$ .<sup>37,38</sup> Yet no physical picture has been proposed by which O atoms transfer between the lattice, diffusing  $O_i$ , the surface, and dissolved  $O_2$ .

The mediating form of adsorbed O remains especially murky. Adsorbed OH (anion and neutral) and molecular  $H_2O$  dominate adsorbate populations on submerged metal oxides,<sup>39–42</sup> but reaction mechanisms for  $O_2$  atop oxides assume participation of adsorbed O,<sup>35</sup> whose existence has been inferred from experiments and density functional theory (DFT) calculations.<sup>43–48</sup> The literature for catalysis and surface science considers O on rutile  $TiO_2$  to sit directly atop a metal cation.<sup>49–56</sup> This species protonates readily. In contrast, DFT calculations for three different oxides<sup>37,57,58</sup> reveal a “surface interstitial” that converts into bulk  $O_i$  by diffusive hopping. The surface interstitial’s high bond coordination implies little propensity for protonation.

Interconversion between these forms of adsorbed O provides the foundation for a self-consistent physical picture to describe atom exchange between the lattice and dissolved  $O_2$ . To support this picture, the present work employs isotopic self-diffusion measurements in submerged rutile  $TiO_2(110)$  single crystals with varying concentrations of  $^{18}O$  isotopic label. We selected the (110) surface termination because extensive literature already exists for this orientation, and its nonpolar structure should minimize surface reconstruction upon immersion.<sup>59</sup> These experiments show that O exchanges between the solid and both dissolved  $O_2$  and  $H_2O$  liquid, mediated within the solid by  $O_i$ . At the surface, DFT calculations suggest that adsorbed O exists in both on-top and surface interstitial configurations. Adsorbed OH appears to provide a single pathway for  $H_2O$  and  $O_2$  to contribute oxygen, although fitting the diffusion data to simple models indicates that  $H_2O$  contributes more. Because rutile  $TiO_2$  is a prototypical metal oxide,<sup>39,60</sup> this picture based on  $O_i$  probably generalizes in many cases to other oxides – explaining important aspects of their thermal, electrochemical, and photochemical reactions with dissolved  $O_2$ .

## 2. Methods

### 2.1 Experiments

Many published experiments seeking to measure participation of lattice O have focused on detecting  $^{18}O$  in the fluid or on the solid surface.<sup>24,32,61</sup> In contrast, the present work focuses on measuring  $^{18}O$  self-diffusion within the solid. Such measurements offer a complementary perspective more directly attuned to defect behavior. Our protocols for the  $^{18}O$  self-diffusion experiments have been detailed previously.<sup>37</sup> The experiments were performed at varying temperatures involving no photochemical perturbations. Undoped single-crystal rutile  $TiO_2(110)$  specimens ( $5 \times 5 \times 0.5$  mm) purchased from MTI Corp. were de-greased by 10 min of ultrasonic agitation in a succession of solvents (acetone, isopropanol, ethanol, and methanol) followed by wet etching (1:2, 30%  $NH_4OH:H_2O$ ) at room temperature for 40 min to remove elemental poisons that inhibit  $O_i$  injection. Surface analysis by X-ray photoelectron spectroscopy

(XPS) showed only Ti, O, and C within the detection limit, both before and after  $O_i$  diffusion. Consistent with previous studies, no variations in surface composition with experimental conditions were observed. Atomic force microscopy (AFM) revealed a root mean square (rms) roughness of  $0.23 \pm 0.03$  nm for as-received  $TiO_2$  and  $0.14 \pm 0.08$  nm after wet etching.<sup>58</sup>

We discovered empirically that, during submersion in water, application of potential bias in a conventional three-electrode cell configuration increases the  $O_i$  injection rate and thereby aids the measurement of profile metrics.  $TiO_2$  specimens were immersed for 60 min at constant temperature ( $70^\circ C$ ) with a potential bias applied using a Biologic SP200 potentiostat. The electrical connection to the  $TiO_2$  specimens was a Cu wire attached with double-stick carbon tape covered with Kapton. An Ag/AgCl reference electrode and a Pt counter electrode were employed. The water contained no electrolyte, and the pH was about 7. Before immersion, 10 min of gas bubbling through the aqueous solution with simultaneous gas flow through the headspace established liquid–gas equilibrium.

The solid  $TiO_2$  was undoped and assumed to be insulating. In addition, no electrolyte was employed, so no faradaic electrochemistry occurred during the experiments. Potentiostat measurements of the current were very small (10–100 nA) and uncorrelated with any profile metric. The potentiostat itself typically displayed an overload warning characteristic of an open circuit. As shown in Fig. S1 of the ESI,<sup>†</sup> measurements of pH before and after each self-diffusion experiment revealed only small changes. The starting pH averaged 6.96 with a standard deviation of 0.30, and the pH change during diffusion was most commonly 0.25 or less.

In water submersion without applied bias, injected fluxes of  $O_i$  are sufficiently high to yield isotopic fractionation within the first few nanometers of the surface.<sup>38</sup> In this region, the concentration of  $^{18}O$  dips below the natural abundance level – a counterintuitive phenomenon, because the ambient solution is enriched in  $^{18}O$ . Fractionation originates from high gradients in  $O_i$  concentration combined with the statistics of diffusion by an interstitialcy mechanism, wherein two O atoms share a single lattice site and either atom can hop into an adjacent site in a diffusive event. The existence of fractionation provides added features in the diffusion profiles for quantifying profile behavior.

To ascertain the relative contributions of  $O_2$  and  $H_2O$  to injection and diffusion of  $O_i$ , the following combinations of isotopic labels and water–gas ambient were investigated:

- Case I: 10%  $^{18}O$ -labeled  $H_2O$  (Sigma-Aldrich), natural abundance  $N_2$  (19 profiles)
- Case II: 10%  $^{18}O$ -labeled  $H_2O$ , natural abundance  $O_2$  (8 profiles)
- Case III: 10%  $^{18}O$ -labeled  $H_2O$ , natural abundance air (74 profiles)
- Case IV: natural O-abundance (0.2%)  $D_2O$  (Sigma-Aldrich), 97% labeled  $^{18}O_2$  (Sigma-Aldrich, 12 profiles)

These four cases contain differing concentrations of  $^{18}O$  in the liquid and gas phases, allowing inference of the source of  $^{18}O$ .



$^{18}\text{O}$  concentration profiles were measured *ex situ* by secondary ion mass spectrometry (SIMS) in time-of-flight mode using a PHI-TRIFT III instrument with a 3 keV Cs ion beam source and a spot size of 0.5 mm.  $^{18}\text{O}$  concentrations were calibrated to the known natural abundance of  $^{18}\text{O}$  (0.2%) in the as-received  $\text{TiO}_2$  specimens. Profiles were measured at 2–5 different locations on the surface of each specimen.

## 2.2 DFT calculations

DFT calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP).<sup>62,63</sup> The bulk rutile  $\text{TiO}_2$  structure was obtained from the Materials Project.<sup>64</sup> The structure was optimized using the Perdew–Burke–Ernzerhof<sup>65</sup> (PBE) generalized gradient approximation (GGA) exchange–correlation functional, and the projector augmented wave<sup>66</sup> (PAW) method was employed. Details of the optimized structure were previously published.<sup>67</sup> For the slab modeling, the (110) plane in its  $2 \times 1$  *in vacuo* reconstruction was employed. Some computational evidence suggests the surface reconstructs to  $1 \times 1$  periodicity upon submersion,<sup>68</sup> but most first principles simulations of this surface upon submersion continue to employ the  $2 \times 1$  structure.<sup>46,56</sup> A plane wave cutoff energy of 520 eV was used, together with Monkhorst–Pack *k*-point sampling having a  $4 \times 4 \times 1$  mesh size. All atoms were relaxed until the forces on each atom were smaller than  $0.01 \text{ eV } \text{\AA}^{-1}$ . The slab thickness was set to  $15.74 \text{ \AA}$  and included five trilayers of (O– $\text{Ti}_2\text{O}_2$ –O) to allow for a net charge-neutral stoichiometry.<sup>57</sup> A vacuum thickness of  $15.0 \text{ \AA}$  was employed to isolate each slab from its images originating from periodic boundary conditions.

To model specific adsorption cases, all potential adsorption sites were examined. The (110) plane includes  $\text{Ti}_{5f}$ ,  $\text{O}_{3f}$  and  $\text{O}_{2f}$  sites, although only the first two lie in-plane and are of direct concern here. Adsorbed O atoms adopt an “on-top” geometry at the  $\text{Ti}_{5f}$  site. At the  $\text{O}_{3f}$  site, adsorbed O atoms can adopt a “dumbbell” geometry (neutral charge) containing an O–O bond or a “split” geometry (–2 charge) that contains bonds only to surrounding metal cations. For the split, we employed a previous protocol<sup>57</sup> that places an O vacancy on the backside of the slab to facilitate adsorbate charging while maintaining the simulation’s Fermi energy ( $E_F$ ) at the top of the valence band. The adsorption energy was computed as described previously,<sup>57</sup> with the oxygen chemical potential computed under standard conditions ( $25 \text{ }^\circ\text{C}$  and 1 atm) for both O-rich ( $\mu_{\text{O}} = -4.68 \text{ eV}$ ) and Ti-rich ( $\mu_{\text{O}} = -10.11 \text{ eV}$ ) environments.

## 3. Results

Fig. 1 illustrates typical  $^{18}\text{O}$  SIMS profiles following diffusion. The general features match those observed previously in the absence of applied potential bias,<sup>37,38</sup> with the most dramatic being the isotopic fractionation represented by the near-surface “valley” wherein the  $^{18}\text{O}$  concentration drops well below natural abundance ( $C_{\text{nat}} = 1.29 \times 10^{20} \text{ cm}^{-3}$ ) as described at length elsewhere.<sup>38</sup> This phenomenon is transient and represents a manifestation of uphill diffusion<sup>69</sup> in the solid state.

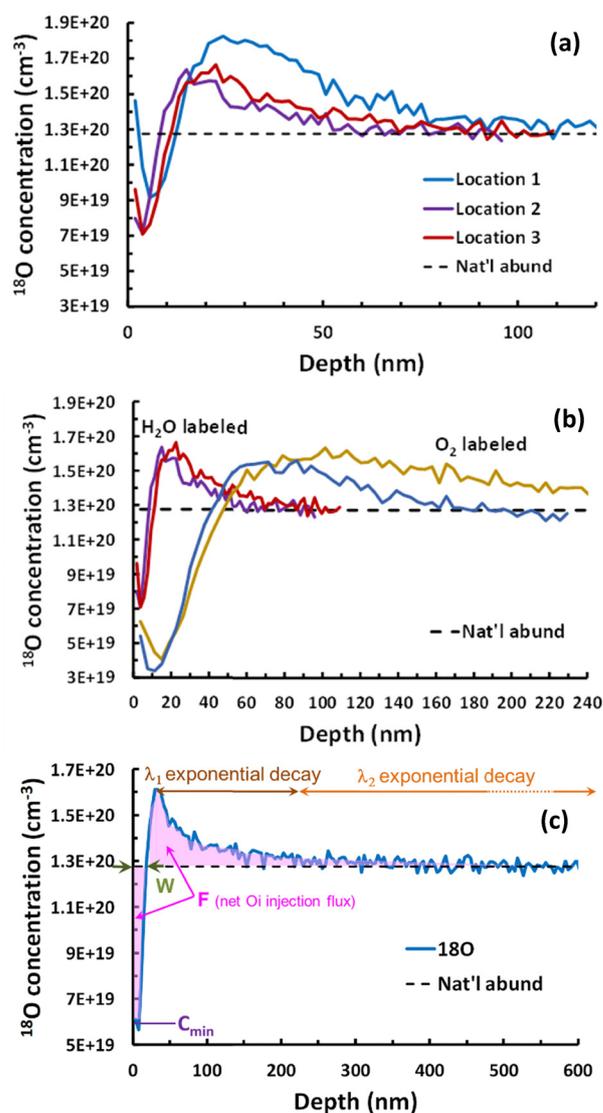


Fig. 1 (a) Example  $^{18}\text{O}$  profiles at several locations on a single specimen of case II ( $\text{H}_2\text{O}$  with 10 at%  $^{18}\text{O}$ ) with  $V_{\text{appl}} = -0.8 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$ ,  $70 \text{ }^\circ\text{C}$ ,  $t = 60 \text{ min}$ , illustrating “valley” regions (having  $^{18}\text{O}$  concentrations below natural abundance). The variability is characteristic as discussed in the text. (b) Example  $^{18}\text{O}$  profiles comparing case II (“ $\text{H}_2\text{O}$  labeled,” 10 at%  $^{18}\text{O}$ ) and case IV (“ $\text{O}_2$  labeled,” 97 at%  $^{18}\text{O}$ ) at  $70 \text{ }^\circ\text{C}$ ,  $t = 60 \text{ min}$ . Although  $V_{\text{appl}}$  varies, this condition does not affect the profiles; the variation has the same origin as in (a). Typical  $\text{O}_2$ -labeled profiles extend much deeper than  $\text{H}_2\text{O}$ -labeled profiles and exhibit deeper and wider valleys near the surface. (c) Example profile showing definitions of the metrics  $W$  and  $C_{\text{min}}$ ,  $F_{18}$ ,  $\lambda_1$  and  $\lambda_2$ . Profile was measured in air (case I) at  $V_{\text{appl}} = -0.4 \text{ V}$ ,  $70 \text{ }^\circ\text{C}$ ,  $t = 60 \text{ min}$ . For all profiles here, the water contained no electrolyte, and was air-equilibrated prior to diffusion by bubbling for 10 min.

All features are stable during long-term storage. Fig. 1a shows examples of profiles for labeled water with natural abundance  $\text{O}_2$  (case II). Details of the profile shapes vary with position on a given specimen. Such variations have been discussed at length elsewhere<sup>58,70</sup> and arise in large part from differences in the level of surface contamination, especially adventitious carbon, which can poison the surface sites that facilitate injection. Fig. 1b shows typical profiles comparing



cases II and IV, wherein the gas ambient is pure O<sub>2</sub> and either the water or the gas, respectively, is isotopically labeled. Differences between the two cases are evident despite the variability; profiles for case IV extend much deeper than case II and exhibit deeper and wider valleys near the surface. This latter behavior seems quite counterintuitive, as greater <sup>18</sup>O enrichment in the gas and no enrichment in the liquid enhances the degree of fractionation.

Fig. 1c illustrates five metrics that were used to quantify the profiles:

- $F_{18}$ : net <sup>18</sup>O<sub>i</sub> injection flux.
- $C_{\min}$ : near-surface minimum of the <sup>18</sup>O concentration in the “valley.”
- $W$ : width of the region for which the <sup>18</sup>O concentration is below its natural abundance.
- $\lambda_1$  and  $\lambda_2$ : characteristic lengths describing bi-exponential decay, with  $\lambda_1 \ll \lambda_2$ .

$W$  and  $C_{\min}$  characterize the extent of isotopic fractionation, while  $\lambda_1$  and  $\lambda_2$  describe the penetration of <sup>18</sup>O into the solid. The ESI<sup>†</sup> details the fitting procedures employed to obtain these metrics.

As shown in Fig. S2 and Table S2 of the ESI,<sup>†</sup> the metrics change regardless of the applied potential's value. The mechanism by which the applied potential bias operates remains unknown. One possibility is that the electrode system unintentionally removes a contaminant that would normally poison injection sites. Alternatively, a form of electrostatic electrochemistry<sup>71,72</sup> operates, wherein redox reactions occur on statically charged insulators. The static charge in published reports is usually created by mechanical rubbing,<sup>73,74</sup> and whether charge transfer involves ions or electrons is still debated. A third possibility is that an electric field enhances injection.

Knowledge of the mechanism is not important for the focus of this work, which seeks to demonstrate the importance of bulk and surface O interstitials in mediating the exchange of O atoms between TiO<sub>2</sub> and the liquid. Bulk and surface interstitials are already known to serve this purpose for TiO<sub>2</sub> in water without applied bias, both thermally<sup>37</sup> and with UV stimulation.<sup>70</sup> As the sections below will show, applying potential bias does not change this picture. Applying bias simply accentuates the profile metrics compared to water without bias, thereby making measurement easier. For example, applying potential bias increases the net injection fluxes by over an order of magnitude, which steepens the gradient for fractionation and greatly extends the penetration of interstitials up to roughly 10 μm into the solid. Accordingly, the <sup>18</sup>O-depleted region's width increases from an average of 2.8 nm

to as high as 90 nm. Isotopic depletion increases from an average factor of 1.4 below natural abundance to as high as 3.

### 3.1 Statistical tests for isotope and O<sub>2</sub> concentration effects

Table 1 shows the mean and standard deviation for each of the five metrics ( $F_{18}$ ,  $W$ ,  $C_{\min}$ ,  $\lambda_1$ ,  $\lambda_2$ ) for the four ambient conditions studied. The results in Table 1 appear as bar graphs in Fig. 2. The variability among profiles induces large standard deviations for each metric. Hence, statistical tests were employed to determine whether changes in the experimental conditions between cases lead to a significant change in the mean. Such tests yield a probability (“*p*-value”) that quantifies the likelihood of the null hypothesis being true. The null hypothesis is that a difference in the mean between two cases arises from random chance.

Histograms of the metric distributions for the largest data set (case III) exhibit considerable deviations from normality even after logarithmic transformation (Fig. S3 and S4 in the ESI<sup>†</sup>). The classical “parametric” Student's *t*-test for comparing means exhibits considerable robustness to deviations from a normal distribution.<sup>75,76</sup> Nevertheless, we also employed a common “non-parametric” Mann-Whitney *U*-test that does not presuppose normality. There is no reason to believe cases I–IV have differently shaped distributions.

In such situations, a non-parametric test compares medians<sup>77</sup> rather than means. However, this difference in data aggregation affects the statistical power of *t* and Mann-Whitney tests (*i.e.*, the likelihood of detecting a statistically significant effect). The values for most of the metrics in Table 1 vary over 1.5 to 2 orders of magnitude (*e.g.*, 0.6 to 94 nm for  $W$ ). The means typically exceed the medians by a factor of 1.3 to 1.6. Thus, closely spaced small values are weighted more heavily than widely spaced large ones in a statistical test that compares medians instead of means. This property decreases the vulnerability of Mann-Whitney tests to type I errors that reject the null hypothesis when it is true but increases their vulnerability to type II errors that fail to reject the null hypothesis when it is false.

Table 2 shows the *p*-values for each metric obtained from *t*-tests and Mann-Whitney *U*-tests for all pairwise permutations of ambient conditions. The comparison of cases II–IV has particular importance because no change occurs in the chemical composition of either gas (pure O<sub>2</sub>) or liquid. Only the isotopic composition changes. Both tests yield *p* < 0.02 for all profile metrics. In other words, the likelihood is very high that changing only the <sup>18</sup>O mole fractions in the gas and liquid (at constant partial pressure of O<sub>2</sub>) suffices to influence all aspects of the

Table 1 Means and standard deviations (in parentheses) of profile metrics

	Case I	Case II	Case III	Case IV
$\bar{F}_{18}$ (cm <sup>-2</sup> s <sup>-1</sup> )	1.6(1.0) × 10 <sup>11</sup>	1.2(0.6) × 10 <sup>11</sup>	3.0(2.9) × 10 <sup>11</sup>	5.1(4.5) × 10 <sup>11</sup>
$\bar{W}$ (nm)	8.3(5.3)	6.1(3.0)	13.6(14.4)	27.5(16.1)
$\bar{C}_{\min}$ (cm <sup>-3</sup> )	7.5(1.8) × 10 <sup>19</sup>	8.3(1.4) × 10 <sup>19</sup>	8.3(2.0) × 10 <sup>19</sup>	4.2(1.0) × 10 <sup>19</sup>
$C_{\text{nat}} - \bar{C}_{\min}$ (cm <sup>-3</sup> )	5.4(1.8) × 10 <sup>19</sup>	4.6(1.4) × 10 <sup>19</sup>	4.6(2.0) × 10 <sup>19</sup>	8.6(1.0) × 10 <sup>19</sup>
$\bar{\lambda}_1$ (nm)	21(14)	17(10)	45(45)	80(79)
$\bar{\lambda}_2$ (nm)	390(270)	240(140)	420(350)	1160(850)



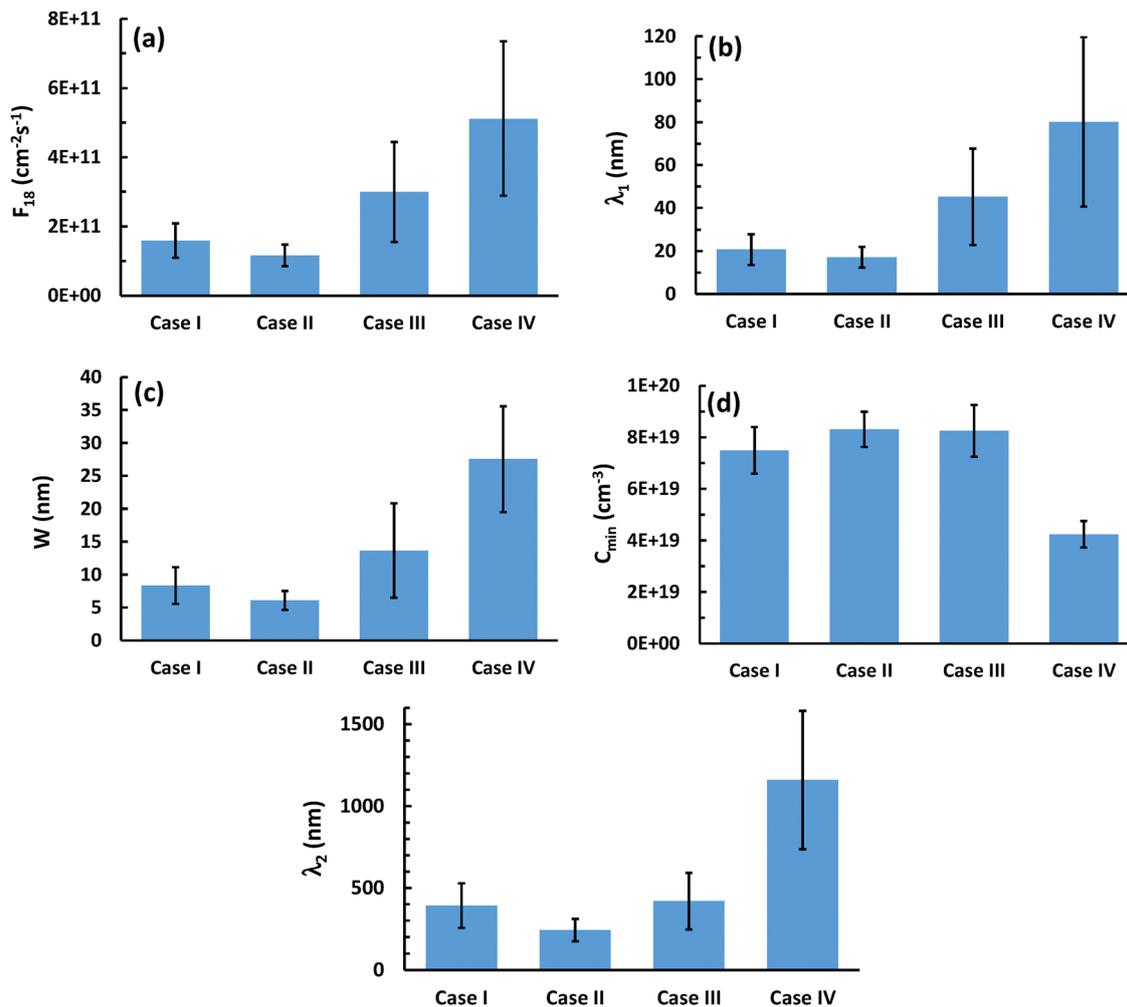


Fig. 2 Bar graphs showing means and standard deviations for profile metrics in each of the four cases: (a)  $F_{18}$  (b)  $\lambda_1$  (c)  $W$  (d)  $C_{\min}$  (e)  $\lambda_2$ . For all metrics, conditions are 70 °C,  $t = 60$  min.

Table 2 Pairwise statistical analyses of five metrics

Ambient pair	$F_{18}$ ( $\text{cm}^{-2} \text{s}^{-1}$ )		$C_{\min}$ ( $\text{cm}^{-3}$ )		$W$ (nm)		$\lambda_1$ (nm)		$\lambda_2$ (nm)	
	$p_{t\text{-test}}$	$p_{\text{MW}}$	$p_{t\text{-test}}$	$p_{\text{MW}}$	$p_{t\text{-test}}$	$p_{\text{MW}}$	$p_{t\text{-test}}$	$p_{\text{MW}}$	$p_{t\text{-test}}$	$p_{\text{MW}}$
Cases I–II	0.19	0.44	0.24	0.33	0.18	0.37	0.47	0.94	0.075	0.19
Cases I–III	$8 \times 10^{-4}$	0.15	0.12	0.45	0.018	0.20	$1 \times 10^{-4}$	0.038	0.73	0.83
Cases I–IV	0.022	$7 \times 10^{-4}$	$9 \times 10^{-7}$	$8 \times 10^{-5}$	$1 \times 10^{-3}$	$2 \times 10^{-4}$	0.027	$6 \times 10^{-4}$	0.010	$6 \times 10^{-4}$
Cases II–III	$4 \times 10^{-5}$	0.087	0.85	0.65	$4 \times 10^{-4}$	0.092	$4 \times 10^{-5}$	0.13	0.011	0.18
Cases II–IV	0.012	$8 \times 10^{-4}$	$1 \times 10^{-5}$	$2 \times 10^{-4}$	$4 \times 10^{-4}$	$4 \times 10^{-4}$	0.019	0.0014	0.0056	$5 \times 10^{-4}$
Cases III–IV	0.14	0.041	$1 \times 10^{-9}$	$4 \times 10^{-4}$	0.011	$1 \times 10^{-3}$	0.17	0.078	0.012	$7 \times 10^{-5}$

$^{18}\text{O}$  profiles. This result shows that  $\text{O}_2$  gas supplies some of the injected oxygen. Furthermore, the effects extend at least as deep as the largest individual value of  $\lambda_2$ , *i.e.*,  $> 1 \mu\text{m}$ .

Cases I, II and III entail no change in isotopic composition of either gas or liquid; only the chemical concentration of  $\text{O}_2$  varies in the gas phase. The  $t$ -test  $p$ -values are rather large for I–II but are quite small for many metrics involving I–III and II–III. The corresponding Mann–Whitney  $p$ -values are noticeably larger for these latter two comparisons. However, the

$p$ -values for  $\lambda_1$  in I–III are quite small at 0.038 and are also rather small for  $F_{18}$  and  $W$  in II–III at 0.087 and 0.092, respectively. In combination, the two tests therefore agree that  $\text{O}_2$  concentration affects some metrics of the profiles.

### 3.2 DFT simulations

Fig. S5 (ESI<sup>†</sup>) shows surface geometries of both pristine and bridging hydroxylated  $\text{TiO}_2(110)$  surfaces. For the bridging hydroxylated surface, two hydrogen atoms occupy bridging



$O_{2f}$  sites to represent the fragments of liquid water dissociation. Fig. 3 displays the metastable surface geometries of O atoms adsorbed on pristine  $TiO_2(110)$ , which include dumbbell, split and on-top structures. The dumbbell and split configurations both associate two O atoms with a surface  $O_{3f}$  site originally occupied by a single O atom. The two atoms represent distorted versions of corresponding  $O_i$  configurations in the bulk reported previously, and thus act like “surface interstitials.”<sup>57</sup> The structures remain minimally changed upon hydroxylation of the surface, as shown in Fig. 4. Table 3 summarizes the calculated adsorption energies and Bader charges in the limit of maximally O-rich conditions investigated here. Adsorption energies

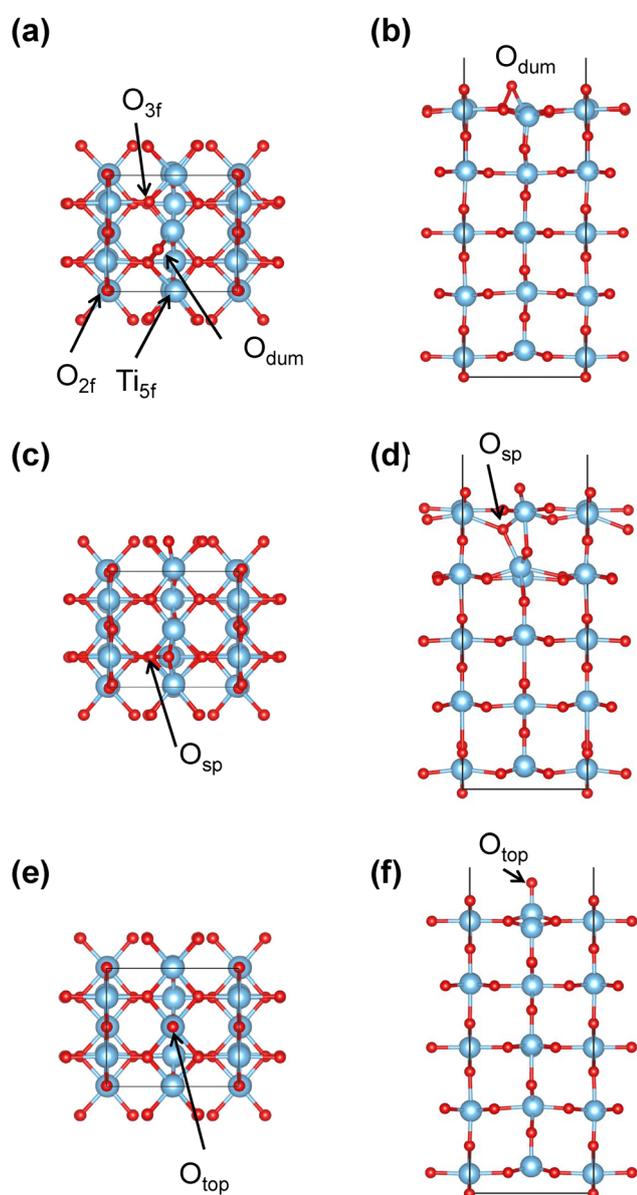


Fig. 3 Geometry of metastable adsorbed O configurations on pristine  $TiO_2(110)$  terraces, including (a) and (b) dumbbell ( $O_{dum}$ ), (c) and (d) split ( $O_{sp}$ ) and (e) and (f) on-top ( $O_{top}$ ). Panels (a), (c) and (e) show top views and (b), (d) and (f) show side views. Shading colors respectively represent blue for Ti and red for O.

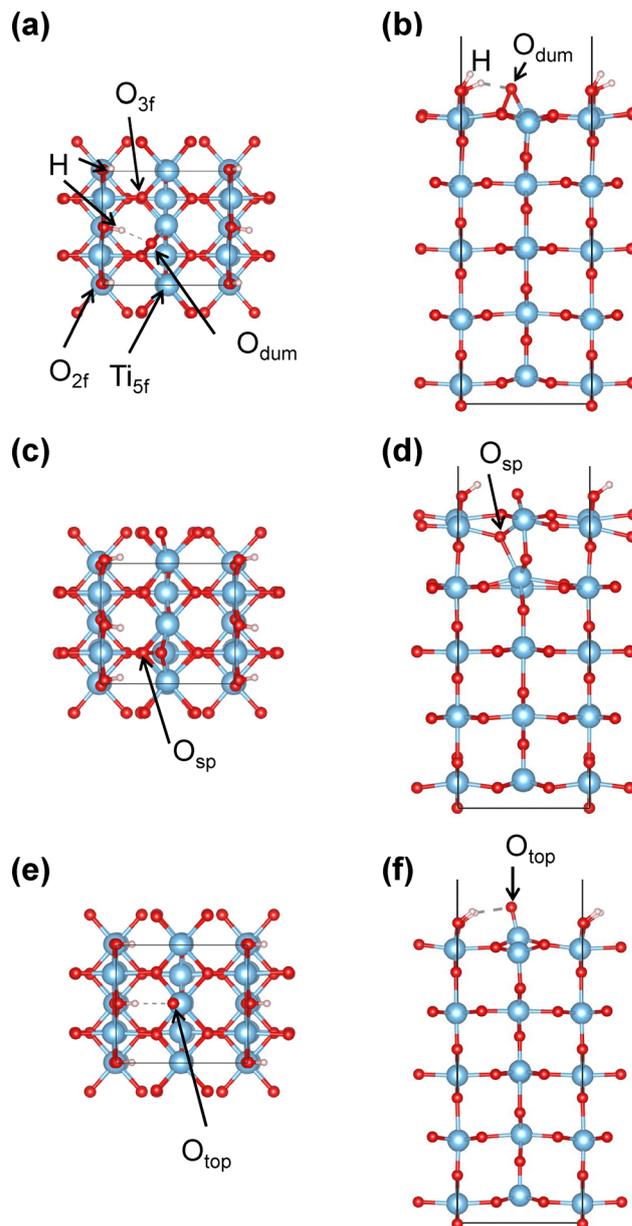


Fig. 4 Geometry of metastable adsorbed O configurations with co-adsorbed bridging hydroxyls on  $TiO_2(110)$  terraces, including (a) and (b) dumbbell ( $O_{dum}$ ), (c) and (d) split ( $O_{sp}$ ) and (e) and (f) on-top ( $O_{top}$ ). Panels (a), (c) and (e) show top views and (b), (d) and (f) show side views. Shading colors respectively represent blue for Ti, red for O, and white for H.

appear for values of  $E_F$  at the valence band maximum (VBM,  $E_F = 0$  eV) and conduction band minimum (CBM,  $E_F = 3.1$  eV). For completeness, Table S3 (ESI<sup>†</sup>) shows parallel results for maximally Ti-rich conditions.

Bader charge analysis of the dumbbell surface interstitial structure on the pristine surface shows  $-0.43e^-$  on the topmost atom and  $-0.69e^-$  on its nearest neighbor just below, for a sum of  $-1.12e^-$ . Previous analysis<sup>57</sup> has demonstrated this species to be neutral. By contrast, the split structure is known to be charged  $-2$ . The topmost atom has a Bader charge of  $-1.11e^-$ , and  $-0.94$  resides on the underlying nearest-neighbor O just



Table 3 Adsorption energy and Bader charge of adsorbed O on TiO<sub>2</sub>(110): O-rich conditions

TiO <sub>2</sub> (110) surface conditions	Adsorption configuration	Adsorption energy (eV)		Bader charge (e <sup>-</sup> )		Charge state
		E <sub>F</sub> = 0 eV	E <sub>F</sub> = 3.1 eV	Adsorbed O atom	Neighboring O atom	
Pristine	Dumbbell	0.80	0.80	-0.43	-0.69	0
	Split	0.95	-5.11	-1.11	-0.94	-2
	On-top	2.63	-0.40	-0.61	-1.09	-1
Bridging hydroxylated	Dumbbell	0.48	0.48	-0.54	-0.71	0
	Split	-0.30	-6.36	-1.12	-1.03	-2
	On-top	-2.21	-5.23	-0.87	-1.13	-1

below for a total of  $-2.05e^-$ . For the on-top geometry, the adsorbed O has a Bader charge of  $-0.61e^-$ . The symmetry of this structure does not associate this O with any particular in-plane atom, but each of the four equivalent O<sub>3f</sub> nearest-neighbor atoms in the surface plane have a Bader charge of  $-1.09e^-$ . Thus, a sum comparable to those of the dumbbell and split configurations is  $-1.70e^-$ , which lies intermediate between the values for the dumbbell and the split. The calculations therefore suggest an on-top charge state of  $-1$ , consistent with previously published DFT results for isolated O.<sup>49</sup> For the hydroxylated surface, the Bader charges all become slightly more electron-rich, but the ordering does not change. Thus, we infer no change in charge state induced by hydroxylation.

For nearly all values of  $E_F$ , the adsorption energies on the pristine surface in Table 3 show that the split geometry is most stable (most negative). The dumbbell becomes most stable by a small margin when  $E_F$  is near the VBM. On the hydroxylated surface, the on-top geometry is most stable for  $E_F$  near the VBM, while the split is most stable for  $E_F$  near the CBM. In contrast with the surface interstitial structures, for the on-top configuration the adsorbed O atom pulls the underlying Ti atom significantly above the surface plane. Fig. 4e and f show that hydroxylation stabilizes the resulting bond stretching by pulling the adsorbed O laterally toward a nearby H atom. Much less stabilization is possible for the surface interstitial structures.

## 4. Discussion

### 4.1 Contributions of injected O from H<sub>2</sub>O and O<sub>2</sub>

The <sup>18</sup>O profiles provide strong evidence that both H<sub>2</sub>O and dissolved O<sub>2</sub> contribute O that diffuses into submerged TiO<sub>2</sub>. Do O<sub>2</sub> and H<sub>2</sub>O contribute independently or employ the same pathway? Adsorbate populations on submerged TiO<sub>2</sub> are dominated by OH (either anion or neutral) and molecular H<sub>2</sub>O.<sup>39–42</sup> Adsorbed OH is not very acidic,<sup>78</sup> yet experiments with deuterated water have shown<sup>37</sup> that oxygen injects as O<sub>i</sub>, not OH. Similar experiments performed here with applied bias yield the same results. This apparent paradox can be reconciled by the capacity for hydrogen bonding<sup>79</sup> and acid–base chemistry<sup>80</sup> afforded by the liquid phase. These solvation effects stabilize intermediates such as adsorbed O,<sup>35</sup> as evidenced by electron spin resonance<sup>81</sup> and photoluminescence.<sup>45</sup> Submersion can reduce the activation energy for O<sub>2</sub> dissociation<sup>82</sup> and increase the acidity of OH<sup>83</sup> by reducing the barrier for deprotonation.<sup>84</sup>

The temperature dependence of O<sub>i</sub> injection in submersion is much less than that of elementary-step injection of adsorbed O, which suggests the rate-limiting step is kinetically upstream.<sup>37</sup> Thus, there is ample reason to believe that deprotonation of OH to O limits the overall rate of O<sub>i</sub> creation, meaning that adsorbed OH serves as a single kinetic conduit for movement of O between the solid and fluid.

Note that solvation effects limit the mechanistic insights afforded by the large literature for *in vacuo* adsorption of H<sub>2</sub>O and O<sub>2</sub> on TiO<sub>2</sub>. As with submerged TiO<sub>2</sub>, those studies show that H<sub>2</sub>O can dissociate on TiO<sub>2</sub> and other common metal oxides. On TiO<sub>2</sub>, surface V<sub>O</sub> aids dissociation by providing adjacent cation and anion sites that bond readily to H<sub>2</sub>O and the products OH and H.<sup>40</sup> However, OH appears as the only oxygenated product<sup>39,61,85</sup> because no solvation is possible to stabilize adsorbed O. Without doping or photoexcitation, molecular O<sub>2</sub> chemisorption *in vacuo* requires electron donation from V<sub>O</sub> or other surface defects.<sup>40</sup> Dissociation of O<sub>2</sub> to O is favored by conditions that increase the electronegativity of the surface,<sup>40,86</sup> including the presence of electron donors such as surface V<sub>O</sub>.<sup>40,50</sup> However, gaseous O<sub>2</sub> does not adsorb and dissociate fast enough on TiO<sub>2</sub>(110) to inject O<sub>i</sub> unless temperatures exceed about 600 °C.<sup>87</sup> In submersion, solvation effects enable dissociation and injection of O<sub>i</sub> even at 70 °C.

The aftereffects of ion sputtering for surface cleaning also limit the direct translation of *in vacuo* mechanistic findings to TiO<sub>2</sub> submersion. Sputtering preferentially removes O from the solid, which chemically reduces some of the Ti and forms V<sub>O</sub>.<sup>40</sup> Reduction of the surface layer is irreversible *in vacuo* below 400 K<sup>40,88</sup> unless the ion fluence is low.<sup>40,89,90</sup> With low fluence, submersion quickly removes surface V<sub>O</sub> with dissolved O<sub>2</sub><sup>40,91,92</sup> or H<sub>2</sub>O itself.<sup>93–95</sup> However, submersion reverses V<sub>O</sub> formation in the near subsurface (2–3 nm) slowly and only partially.<sup>96</sup> This failure to reverse subsurface reduction reflects the suppression of Ti interstitials, which are central to *in vacuo* reversal of chemical reduction above 400 K.<sup>88</sup> Ti interstitials play no role at submersion temperatures because there is no generation mechanism, and their high mobility ensures their sequestration in bulk traps or at the surface.<sup>97</sup>

Two mathematical models were formulated and compared to test the hypothesis that OH serves as a single kinetic conduit for O. Model derivations appear in the ESI.† One model is agnostic about the injection mechanism (thereby not aligning with the hypothesis) and assumes that H<sub>2</sub>O and O<sub>2</sub> contribute O<sub>i</sub> and isotopic labels in linear proportion to their respective



total concentrations in the fluid. The net injection flux  $F_{18}$  of  $^{18}\text{O}$  (time-averaged) is then given by:

$$F_{18} = Y_{18,W}x F_W + Y_{18,O_2}X_{O_2}(1-x)F_W, \quad (1)$$

where  $Y_{18,W}$  and  $Y_{18,O_2}$  respectively denote the mole fraction of  $^{18}\text{O}$  in water and  $\text{O}_2$ ,  $X_{O_2}$  denotes the chemical mole fraction of  $\text{O}_2$  (all isotopes) in the gas,  $x$  denotes the fraction of injected O originating from  $\text{H}_2\text{O}$ , and  $F_W$  is the net injection flux of O if only water supplies the oxygen.

The second model aligns with the hypothesis by presupposing a Langmuir-style dual pathway mechanism wherein both  $\text{O}_2$  and  $\text{H}_2\text{O}$  inject through the same adsorbed OH intermediate whose surface coverage does not vary. This differs slightly from “competitive adsorption,” wherein  $\text{O}_2$  and  $\text{H}_2\text{O}$  compete for the same surface sites but have different coverages. For simplicity, first order kinetics are assumed for dissociative adsorption and desorption of  $\text{H}_2\text{O}$  and  $\text{O}_2$  to form adsorbed O. First order kinetics are also assumed for conversion of OH to injected O. The rate constant  $k_{\text{inj}}$  for injection is a composite quantity that implicitly contains the rate constants for deprotonation of OH and injection of O, and the concentration of adsorbed O. The resulting expression for  $F_{18}$  is:

$$F_{18} = k_{\text{inj}}\theta_{\text{OH},18} = k_{\text{inj}} \left[ \frac{Y_{18,W}x + Y_{18,O_2}X_{O_2}(1-x)}{x + X_{O_2}(1-x)} \right]. \quad (2)$$

In the asymptotic limit of  $x = 1$ , eqn (1) from the linear proportion model represents a limiting case of eqn (2) from the dual pathway model with  $F_W = k_{\text{inj}}$ . The dual pathway model has the same number of fitting parameters (two) as the linear proportion model but allows for possible “saturation” of adsorbed OH with gas-derived O as the  $\text{O}_2$  concentration rises. Thus, fitting eqn (1) and (2) to the means values from experiments offers a direct comparison with the same number of fitting parameters of two different models: one that allows for saturation and one that does not.

Linear regression using the linear proportion model yields  $x = 0.78$ ,  $F_W = 2.5 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ , and a total residual variance of  $1.9 \times 10^{22} \text{ cm}^{-4} \text{ s}^{-2}$ . Nonlinear regression using the dual pathway model yields  $x = 0.76$ ,  $k_{\text{inj}} = 2.2 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ , and a total residual variance of  $1.5 \times 10^{22} \text{ cm}^{-4} \text{ s}^{-2}$ . The factor of  $10^{22}$  in the variances can be removed by choosing different units or scaling. The point of comparison centers on the multiplying factors 1.5 vs. 1.9. The difference is modest, but the lower residual fitting error for the dual pathway model is consistent with the hypothesis that adsorbed OH provides the single conduit by which O exchanges between fluid and solid.

The two models yield nearly identical values for  $x$ . This factor almost certainly varies with temperature, pH and other experimental variables. Although  $\text{H}_2\text{O}$  provides most of the injected O in the present experiments,  $\text{O}_2$  also contributes significantly. Notably, the concentration of dissolved  $\text{O}_2$  at  $70^\circ\text{C}$  is only  $0.83 \times 10^{-3} \text{ mole l}^{-1}$ , while the concentration of  $\text{H}_2\text{O}$  is  $6.5 \times 10^4$  times higher at  $54.2 \text{ mole l}^{-1}$ . Therefore, the reaction rate constant to form injectable O *via* adsorbed OH must be considerably lower for  $\text{H}_2\text{O}$  than for  $\text{O}_2$ , which is

consistent with chemical intuition that  $\text{H}_2\text{O}$  is much less reactive than  $\text{O}_2$ .

## 4.2 Role of bulk $\text{O}_i$ in lattice O participation

As discussed elsewhere,<sup>37</sup> the diffusive penetration of  $^{18}\text{O}$  to hundreds of nanometers at  $70^\circ\text{C}$  is very strong evidence that the diffusing species is  $\text{O}_i$ . At this temperature,  $V_{\text{O}}$  does not diffuse quickly enough to penetrate that far. The dominance of  $\text{O}_i$  implies that  $V_{\text{O}}$  has been eliminated by  $\text{O}_i$  annihilation, both at the surface and within the bulk.<sup>37</sup>

The prevalence of  $\text{O}_i$  to depths of hundreds of nanometers indicates that lattice O from these depths exchanges with O from both  $\text{H}_2\text{O}$  and dissolved  $\text{O}_2$ . This can be seen as follows. In  $\text{TiO}_2$ ,<sup>67,87,98</sup>  $\text{O}_i$  comprises two atoms symmetrically arranged around a single O lattice site. The atoms assume either a neutral “dumbbell” geometry with an O–O bond, or a charged “split” geometry with bonds only to surrounding metal cations. Diffusion of  $\text{O}_i$  occurs by an interstitialcy mechanism, in which each constituent atom has a 50% chance of hopping – leaving its partner behind in the lattice. Although the net flow of  $\text{O}_i$  is toward the deep bulk, numerous random hopping and lattice exchange events enable some O atoms from the deep bulk to reach the surface for transfer to the fluid.

Several factors drive  $\text{O}_i$  creation at the surface. Some driving forces are energetic, impelled by defect reactions. An example is annihilation of  $V_{\text{O}}$  by  $\text{O}_i$ , which oxidizes the solid. Other examples include addition of  $\text{O}_i$  to extended defects<sup>99</sup> and combination with adventitious hydrogen to form  $\text{O}_i\text{--H}_i^-$  (ref. 37) or other small clusters.<sup>57</sup> Another driving force is entropic. At  $70^\circ\text{C}$ , the solid initially contains virtually no  $\text{O}_i$  because this species has sufficient mobility to disappear at trap sites or the surface. The fluid maintains a continuous supply of adsorbed O, which converts into  $\text{O}_i$  with a modest barrier near  $0.8 \text{ eV}^{29}$  and spreads entropically into the solid.

The rate of  $\text{O}_i$  generation observed here may be compared to the rate of a typical reaction involving  $\text{O}_2$  on  $\text{TiO}_2$  – the OER in photostimulated water splitting, which several groups have investigated on electrically conductive rutile  $\text{TiO}_2(110)$ .<sup>45,100–103</sup> Photocurrents range from  $0.54$  to  $2.2 \text{ mA}\cdot\text{cm}^{-2}$  under UV irradiation in the range from  $0.2$  to  $7 \text{ mW}\cdot\text{cm}^{-2}$ . These photocurrents correspond to  $\text{O}_2$  molecular fluxes in the range  $1\text{--}3 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ . Here,  $F_W$  or  $k_{\text{inj}}$  set the rough magnitude the  $\text{O}_i$  injection fluxes – roughly three orders of magnitude lower. None of the photocurrent studies estimated their current efficiency, so competing reactions could have contributed to the measured current. However,  $\text{O}_i$  injection seems to constitute only a minor side reaction.

## 4.3 Role of a “surface interstitial” in lattice O participation

Adsorbed O on  $\text{TiO}_2(110)$  is usually depicted as sitting directly atop an underlying  $\text{Ti}_{5c}$  atom based on *in vacuo* scanning probe experiments<sup>49–55</sup> and first principles simulations<sup>49,50,52–55</sup> including in submersion.<sup>46,56</sup> The charge state can be toggled between  $-1$  and  $-2$  with a scanning probe tip,<sup>53–55</sup> and this species has been represented in DFT simulations as both  $-1$ <sup>56</sup> and  $-2$ .<sup>46</sup> The present DFT calculations make plausible the hypothesis that both on-top and surface interstitial



(neutral dumbbell and charged split) configurations are metastable. The dominant form depends upon the value of  $E_F$ , the presence of liquid water, the energy barriers for interconversion, and other factors.

The on-top configuration is readily protonated. Protonation of the surface interstitial was not investigated here, but its high bond coordination implies little propensity for this reaction. Under some conditions the on-top and surface interstitial forms could coexist in comparable concentrations. Thus, there is good reason to believe that O moves from the fluid into the solid by a pathway in which  $H_2O$  or  $O_2$  form OH. O atoms produced by  $O_2$  dissociation convert rapidly to OH before injecting; in other words, equilibrium between OH and O greatly favors OH. However, that equilibrium involves the on-top form of O. Some of that form converts into the surface interstitial, which then injects as  $O_i$ . Diffusion of  $O_i$  into the solid ensues, followed by exchange into the lattice. Movement of O from the lattice into the fluid occurs through the reverse of these steps as depicted in Fig. 5.

This mechanistic picture can only be considered plausible, not proven. The present calculations simulate neither free water molecules nor the possibilities for hydrogen bonding

and protonation. Water molecules in the liquid probably screen hydrogen bonding interactions across rows, which seem especially effective at stabilizing the on-top structure. Moreover, liquid water changes relative stability in other ways, such as affecting the value of  $E_F$  at the surface *via* pH or dissolved ions that adsorb.

The foregoing discussion highlights a conceptual disconnect between computational simulations of adsorbed O focused on catalysis, photocatalysis and electrochemistry *vs.* those focused on defect reaction and diffusion in the solid. The former simulations typically emphasize mechanisms involving  $V_O$ , with little explicit consideration of  $E_F$  in the solid. The latter simulations emphasize  $O_i$  but treat liquid solvation and pH simplistically if at all. Both approaches yield useful insights, but further progress must account for contributions to the surface thermodynamics and kinetics from both the liquid and solid.

#### 4.4 Surface sites active for $O_i$ production

What kinds of surface sites other than  $V_O$  promote dissociation of  $H_2O$  and  $O_2$  in submersion? Clues come from fully amorphous metal oxides, which enhance activity for the OER through a wide variety of surface site geometries and their structural flexibility. Such sites are unfortunately difficult to characterize,<sup>104</sup> which is scientifically unsatisfying.<sup>61</sup> However, the design of “high-entropy” oxides embraces such complexity by adding five or more dopant metals to tune the behavior of active sites.<sup>23</sup> With rms surface roughness of  $0.14 \pm 0.08$  nm, the etched  $TiO_2$  employed here also supports ill-defined sites having a wide range of effectiveness for injecting  $O_i$ .<sup>58</sup>

What accounts for the susceptibility of  $TiO_2$  to poisoning of  $O_i$  creation? The most reactive sites on catalytic surfaces are often most vulnerable to deactivation by poisoning.<sup>105</sup> An example afflicts  $TiO_2$  photocatalysts used for the ORR to degrade aqueous pollutants,<sup>8,106,107</sup> wherein the poisons derive from dissolved organic matter. Deprotonation of OH and subsequent injection of  $O_i$  entails a form of heterogeneous catalysis, and a similar correlation between injection activity and poisoning susceptibility appears to hold for injection of  $O_i$  from oxide surfaces.<sup>58</sup>

#### 4.5 Implications for other oxides and reaction conditions

Because rutile  $TiO_2$  is a prototypical metal oxide, this picture based on  $O_i$  probably generalizes in many cases to other oxides – explaining important aspects of their thermal, electrochemical, and photochemical reactions with dissolved  $O_2$ . Examples include oxides fabricated to be hyperstoichiometric, including spinel ferrites,<sup>108–111</sup> perovskites,<sup>112</sup> and Ruddlesden–Popper oxides.<sup>29,30,113–115</sup> Hyperstoichiometric oxides permanently contain mobile  $O_i$ , and often exhibit enhanced catalysis and photocatalysis rates.<sup>29,30</sup>

In stoichiometric oxides,  $O_i$  adopts dumbbell or split configurations like those within  $TiO_2$  in wurtzite  $ZnO$ ,<sup>116–121</sup> corundum  $Al_2O_3$ ,<sup>122–124</sup> fluorite  $CaF_2$ ,<sup>125</sup> corundum  $Cr_2O_3$ ,<sup>126</sup> hematite  $Fe_2O_3$ ,<sup>127,128</sup> perovskite  $SrTiO_3$ ,<sup>129–131</sup> fluorite  $ThO_2$ ,<sup>125,132</sup> fluorite  $UO_2$ ,<sup>133,134</sup> tetragonal<sup>135</sup> and cubic  $ZrO_2$ ,<sup>136,137</sup> and

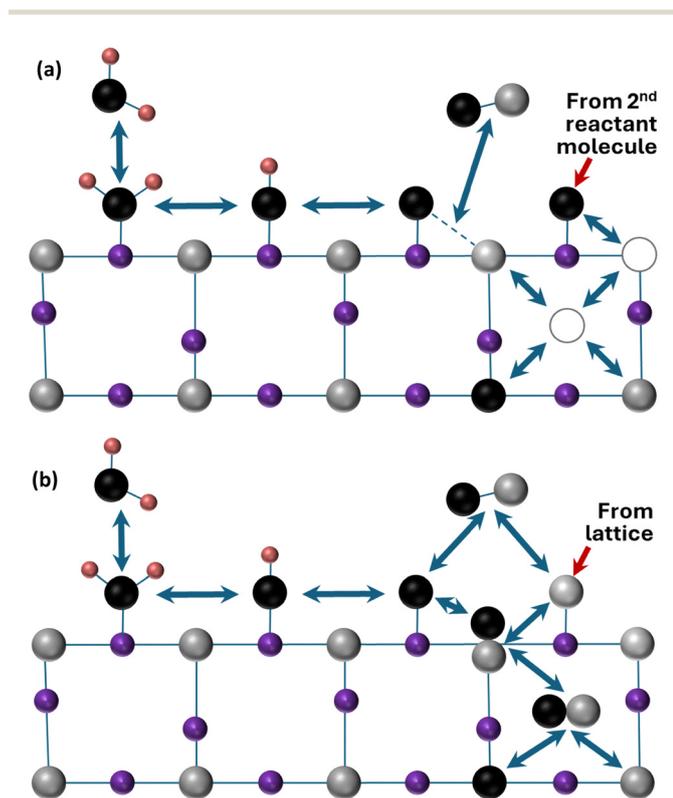


Fig. 5 Schematic comparison of O atom exchange between rutile  $TiO_2(110)$  and  $H_2O$  or dissolved  $O_2$  in the fluid – mediated by (a) O vacancies in the conventional picture and (b) O interstitials in the proposed picture. Diagrams do not attempt to represent exact geometric configurations or certain details of reaction stoichiometry, e.g., the fate of H or exchange of O between mobile species and the lattice. Balls depict atoms of Ti (purple) H (pink) and O originating primarily from the fluid (black) or solid lattice (grey). In reality, atoms originating from the fluid and solid are represented to some degree in all reaction and diffusion pathways.



Ruddlesden–Popper oxides.<sup>138</sup> Following the behavior of TiO<sub>2</sub>, the formation energy for O<sub>i</sub> in these oxides is typically lower than for V<sub>O</sub> in O-rich environments,<sup>87,117,130,139,140</sup> as is the O<sub>i</sub> hopping barrier.<sup>37,141</sup> To existing barrier compilations, low barriers for O<sub>i</sub> hopping (0.13–0.47 eV) may be added for corundum Cr<sub>2</sub>O<sub>3</sub>,<sup>126</sup> hematite Fe<sub>2</sub>O<sub>3</sub>,<sup>128</sup> perovskite SrTiO<sub>3</sub>,<sup>129</sup> fluorite ThO<sub>2</sub>,<sup>125</sup> and fluorite UO<sub>2</sub>.<sup>142</sup>

Counterintuitively, O<sub>i</sub> may mediate aqueous reactions of O even in reduced oxides. The high diffusional mobility of O<sub>i</sub> would make its dominance temporary and difficult to detect. Thus, O<sub>i</sub> may dominate near the surface of vacancy-rich perovskites during reaction and then be replaced by V<sub>O</sub> from the bulk after the reaction ends. Such behavior would accord with the malleability and rapid reversibility of perovskite surface composition and structure observed in other contexts.<sup>32</sup>

## 5. Conclusions

Isotopic self-diffusion measurements in submerged rutile TiO<sub>2</sub> single crystals with varying concentrations of <sup>18</sup>O isotopic label show that O exchange occurs between rutile TiO<sub>2</sub>(110) and dissolved O<sub>2</sub> as well as the H<sub>2</sub>O liquid. Diffusion in the TiO<sub>2</sub> is mediated by oxygen interstitials (O<sub>i</sub>). First-principles calculations strongly suggest that adsorbed O in on-top and “surface interstitial” configurations mediate the surface reaction rather than V<sub>O</sub>. Adsorbed OH appears to provide a single pathway for H<sub>2</sub>O and O<sub>2</sub> to contribute injectable oxygen, although fitting the diffusion data to simple models indicates that H<sub>2</sub>O contributes more. The most active sites on the surface for OH deprotonation and O<sub>i</sub> injection are probably ill-defined and vulnerable to deactivation by poisoning. Compared to the rate of a typical reaction between O<sub>2</sub> and TiO<sub>2</sub> such as photostimulated OER, the rate of O<sub>i</sub> injection is small. Because rutile TiO<sub>2</sub> is a prototypical metal oxide, this physical picture helps to explain many aspects of thermal, electrochemical, and photochemical reactions between dissolved O<sub>2</sub> and a variety of oxides.

## Data availability

The data that support the findings of this study are included within the article and its ESI.†

## Conflicts of interest

There are no conflicts to declare.

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