

Assigning the (1×2) surface reconstruction on reduced rutile by first-principles energetics

Simon D. Elliott^{1,*} and Simon P. Bates^{2,†}¹*Department of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland*²*Department of Physics and Astronomy, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom*

(Received 27 November 2001; published 11 June 2002)

The first systematic survey of the surface structure of reduced rutile TiO_{2-x} by first-principles calculations is reported. Motivated by the reconstructions observed in experiment, rows of ions are considered on the (110) surface so as to satisfy (1×2) periodicity. The surface is reduced by the removal of one O anion per (1×2) cell and over 100 reconstructed surfaces are computed with cations at both bulk and interstitial sites. These spin-polarized density-functional calculations reveal that the most stable reconstruction is the “added row” $+\text{Ti}_2\text{O}_3$ structure of Onishi and Iwasawa [*Surf. Sci.* **313**, L783 (1994)], at a surface energy of $3.29 \pm 0.08 \text{ J m}^{-2}$. We describe this as a twinned dislocation, stabilized by relaxation of the cations away from the surface. All other reconstructions are computed to be at least 0.3 J m^{-2} less stable; many of these feature rutilelike Ti-O half ribbons and rocksaltlike dislocations. Some of these may account for less stable (1×2) surface phases.

DOI: 10.1103/PhysRevB.65.245415

PACS number(s): 68.35.Bs, 68.47.Gh, 73.20.-r

I. INTRODUCTION

A. Aim and layout

The (110) face of rutile TiO_2 has become the prototypical surface in the study of transition metal oxides. It boasts a considerable body of high-quality experimental data,^{1–25} which demonstrate the complexity of the surface chemistry of oxides and raise many interesting questions.

One of these open questions is the subject of the current work: controversy still surrounds the (1×2) pattern ($x = [001]$, $y = [\bar{1}10]$, $z = [110]$) which many groups observe on the reduced rutile (110) surface.^{4,5} While structural models have been proposed to account for this (1×2) pattern, definitive evidence for any one model is still lacking. It is our aim to systematically survey the reduced surface for possible structures that show (1×2) periodicity and assess quantitatively their stability using first-principles calculations. We will thus be able to assign the atomic structure that leads to the (1×2) pattern.

Reconstructions with the stoichiometry TiO_2 were presented in the first part of our study.²⁶ However, it is on reduced crystals TiO_{2-x} that the (1×2) pattern is observed in experiment. The current work, therefore, considers systems with a concentration of one O vacancy per (1×2) surface cell. As we are interested in (1×2) features, the surface reconstructions comprise $[001]$ rows repeating every two $[\bar{1}10]$ units. There are thus four classes according to slab stoichiometry: $(\text{Ti}_{4N}\text{O}_{8N-1})(\text{TiO}_2)_m$, $m = -1, 0, 1, 2$ and we consider slabs $N = 2, 4, 6$ layers thick.

Computational work to date on this reduced (1×2) reconstruction has comprised little more than structural optimizations of candidate models, confirming merely that they represent local energetic minima.^{6–8} To investigate the global energetics is much more difficult and has only been attempted in one case of which we are aware.²⁷ A more systematic approach is taken in the current work, where we survey as many low-energy isomers as possible, using a computational method, which we showed in Ref. 26 to be

efficient but reliable (see Sec. II A). Another important aspect of our earlier work was establishing an accurate way to estimate surface energies. We found that slabs of different formulas can be compared via their surface energies to a precision of about 0.1 eV per cell (0.04 J m^{-2}).²⁶

The paper is laid out as follows. Our notation is introduced in Sec. I C. The (1×2) measurements and models that motivate this study are presented in Secs. I B and I D. The computational method is detailed in Sec. II, along with aspects of the modeling strategy—exactly following Ref. 26 so as to allow close comparison. General energetic considerations (Sec. III A) are followed by specific geometric and energetic results for four types of reconstruction (Secs. III B–III E). The computed data are interpreted and rationalized in the context of experimental data in Sec. IV. Finally, Sec. V contains our conclusions.

B. (1×2) reconstructions

This study is motivated by the (1×2) reconstructions observed on reduced surfaces of rutile TiO_2 . Repeated sputtering and UHV annealing from $>1000 \text{ K}$ gives a deep blue reduced crystal, on which $[001]$ line defects occur on the (110) surface and accumulate to give a (1×2) pattern ($x = [001]$, $y = [\bar{1}10]$), as observed in atomic force microscopy (AFM),^{1,2} low-energy electron diffraction (LEED), and scanning tunneling microscopy (STM).^{3–25} As reduction is likely to occur by loss of O to the vacuum, this surface feature is assumed to be TiO_{2-x} . There is still uncertainty about the structure of the (1×2) reconstruction. Experimental data provide the following criteria, which a model for the reduced reconstruction must satisfy.

$[001]$ strands accumulate to give an ordered (1×2) LEED. In both AFM (Ref. 2) and STM (Ref. 9) such strands are imaged $13 \text{ \AA}$ apart along $[\bar{1}10]$, terminating in a bright feature.^{10,11}

The reconstruction is resolved into a double row,^{6,9,12,13} with the two ridges $y = 3.2 \pm 0.2 \text{ \AA}$ apart in AFM,² and $y = 3.5 \text{ \AA}$ apart in STM.¹²

AFM images the double row at $z=3.0$ Å (just below a full layer: $z=3.3$ Å), with lower outer rows ($z=1.5$ Å) that are displaced by $c/2$ along [001].²

STM corrugations may be less reliable, because of mixed Ti-O character of the empty bands. The (1×2) reconstruction is apparently $z=2.0$ Å high in STM,¹² but under other conditions an STM height of 2.5 Å is reported.⁶

In an oxygen ambient, the reconstruction is observed by STM to grow along [001] on top of (1×1) terraces.¹¹ The center of the double row is in registry with Ti-assigned bright ridges of the lower terrace in STM,¹⁴ and with O-assigned ridges of the upper terrace in AFM.¹

Ion desorption experiments show that the exposed O atoms of this feature are not attached perpendicularly to the surface.¹⁵

The reconstructed surface is stable against acetate-induced reconstruction.¹⁵

Many other reconstructions of rutile (110) have been reported and some of these may be related to the (1×2) reconstruction. For example, a (1×3) reconstruction with a brighter central row has been observed.⁶ There may be two types of reduced reconstruction: noncrosslinked (1×2) and crosslinked (12×2) , the former being stable against O_2 .^{11,16} During reoxidation of the latter, growth of successive layers with alternating (1×1) and (1×2) patterns has been observed by STM.^{11,17} Dark strings (1.3 Å high) constrain growth until they are surrounded and they disappear.¹¹ STM experiments have shown more complex rosettes, rings, and local (2×2) units.^{3,7,10}

As these experiments aim to produce a conducting and nonstoichiometric crystal, it is not surprising that the composition of the crystal is seen to vary with preparation conditions, with a corresponding variation in surface morphology and reactivity. Nevertheless, observation of a (1×2) pattern on the reduced surface is widespread and so it is on this feature that we concentrate.

Despite achieving atomic resolution, STM topographs are not unambiguous. Most of the studies on rutile are at positive sample bias, so that tunneling is from the tip into virtual electronic bands of the sample. The slight differences in spatial extent of these bands across the surface are converted into the STM topograph. Clearly, it is hard to capture the quantum mechanics of these bands in simple intuitive arguments, particularly in the case of a reduced sample of ionic-covalent oxide (partially occupied Ti: d). It thus remains unclear which bright spot in STM corresponds to which ion and there is some debate over the structure of the (1×2) reconstruction. In Sec. I D three of the candidate models for the reconstruction are presented briefly and these are reviewed in the light of our computed models in Sec. IV A.

C. Notation

The rutile isomorph of bulk TiO_2 is a fairly open structure of Ti cations in a distorted hcp O anion sublattice, with empty octahedral interstices forming channels along [001]. As in Ref. 26 we identify a total of four types of cation site: Ti(bh), Ti(bv), Ti(ih), and Ti(iv). The following brief explanation of this notation is aided by reference to Fig. 1. Cations

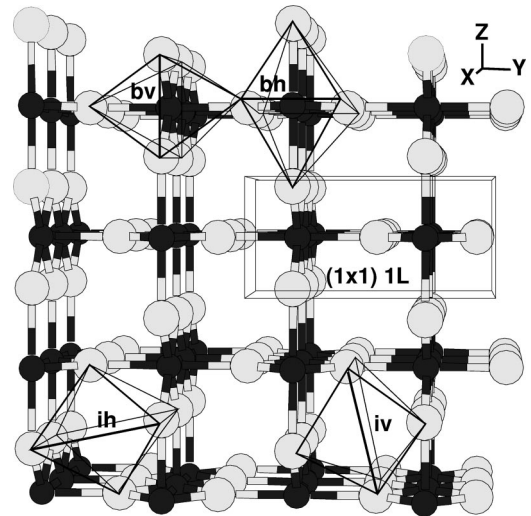


FIG. 1. The structure of bulk rutile TiO_2 aligned with $x=[001]$, $y=[1\bar{1}0]$, $z=[110]$; small dark Ti, larger light O. The box encloses a (1×1) layer containing Ti_2O_4 . Possible cation sites are labeled using distorted octahedra, which are aligned horizontally (h) and vertically (v) in bulk (b) and interstitial (i) positions.

in each unreconstructed (110) layer occupy two types of distorted octahedral site, with the four shorter equatorial Ti-O forming edge-linked [001] “rutile ribbons” in each case.²⁸ If the rutile ribbons are in the (110) plane, we term the octahedral site “bulk horizontal” relative to (110): Ti(bh). On the other hand, if the ribbons are in the $(1\bar{1}0)$ plane, the cation sites are termed “bulk vertical:” Ti(bv).⁶⁰ Rutile layers are separated by empty interstices. The anions bordering these interstices are also approximately horizontal or vertical relative to (110), so that we identify horizontal and vertical cation sites within the interstices: Ti(ih), Ti(iv). Other authors label these cation sites as, respectively, “between” or “adjacent” to anions.²⁹

In the experiments on reduced rutile in which (1×2) reconstructions are observed (Sec. I B) there is no definitive information about the level of nonstoichiometry. All of the candidate models presented in Sec. I D assume a TiO_{2-x} surface missing one O per (1×2) cell. We make the same reasonable assumption and limit our study to surfaces with single O loss per (1×2) cell, which we denote by $\square_O$.

In our earlier notation,²⁶ a single stoichiometric (110) layer ($\nearrow$) is formed by a plane of Ti^{4+} and associated O^{2-} anions in the plane and bridging it, above and below: for example, a Ti_4O_8 unreconstructed (1×2) cell (see Fig. 1). Extending this notation, Ti_4O_7 is a (1×2) $\nearrow$ reduced by the loss of a single O atom and is denoted $1/\square_O$. The smallest stoichiometric unit that may be added to or subtracted from a rutile surface is TiO_2 and represents one quarter of a (1×2) layer ($0.25\nearrow$). We, therefore, group the possible (1×2) reduced reconstructions into four classes by chemical formula: $\pm 0/\square_O$, $+0.25/\square_O$, $+0.5/\square_O$, $-0.25/\square_O$. The notation is arbitrary, since $+0.5/\square_O$ is the same as $-0.5/\square_O$ and $+0.25/\square_O$ is the same as $[\pm 0/\nearrow + TiO]$.

D. Candidate models from literature

Removal of suprasurface bridging O from a bulk-terminated surface has always been a favored model for

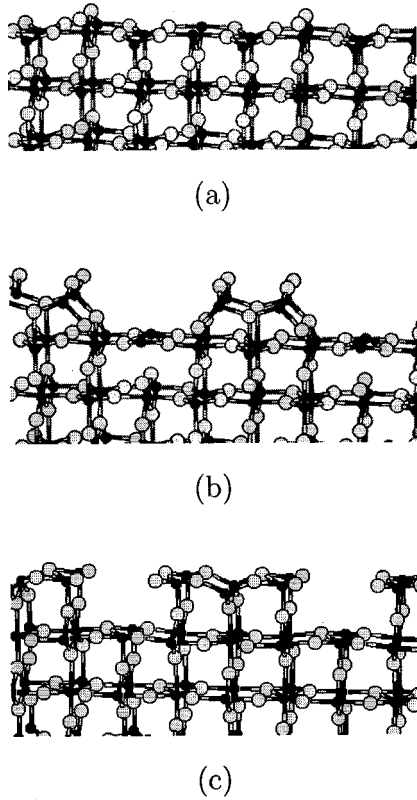


FIG. 2. Models proposed in the literature for (1×2) -reconstructed rutile (110): (a) missing O row (1×2 reduced),¹⁸ (b) added Ti_2O_3 (1×2 reduced),¹² (c) added Ti_3O_5 row (1×2 reduced).^{10,6,4}

reduction.³⁰ The simple “missing row” model of Möller and Wu assumes removal of alternate bridging O so as to give a (1×2) pattern [Fig. 2(a)].¹⁸ Modified versions feature relaxation of surface Ti as well.^{10,19} The missing-row model is generally discounted as it does not match the measured properties of the (1×2) surface. It does not resemble a double added row and desorption of oxygen would be normal to the surface. Earlier computational work on this model confirms that it is unlikely to be the most stable (1×2) reduced surface.³¹ Nevertheless, this model is a popular subject for calculation.^{32–37} Our results for this essentially bulk-terminated structure and other disruptions of the O sublattice are presented in Sec. III C.

Onishi and Iwasawa propose a double row of added Ti_2O_3 , symmetrically disposed about the Ti(bh) site of the layer below, with cations occupying vertically oriented interstices.¹² We denote this reconstruction by $+\text{Ti}(\text{iv})_2\text{O}_3$ [Fig. 2(b)]. This model fits all experimental criteria. The protruding bridging O’s account both for the double strands imaged in STM and the off-normal two-lobe ion desorption. The $+\text{Ti}(\text{iv})_2\text{O}_3$ model has received support from other rutile (110) STM studies,^{9,3,7,8} from STM of adsorbed DCOO (Ref. 14) and from three-layer local density approximation (LDA) calculations.²⁷ Perhaps the strongest support comes from AFM. In one AFM study, (1×2) patterns are imaged as two bright rows with two faint outer rows and an argument for (1×3) patterns due to $\text{Ti}(\text{iv})_2\text{O}_3$ is advanced.² In

another, double rows are interpreted as being in between bridging O of a (1×1) upper terrace.¹ Calculated geometry and energetics of this reconstruction are presented in Sec. III B and discussed in Sec. IV C.

Another bulk-terminated structure is the “added Ti_3O_5 row” of Murray and co-workers^{10,6} [Fig. 2(c)]. We describe this as $-\text{Ti}(\text{bv})\text{O}_2-\text{O}$. In this model, the dark rows in STM are due to alternate missing $\text{Ti}(\text{bv})\text{O}_2$, while laterally relaxed $\text{Ti}(\text{bh})$ are imaged as the bright double row. The central four-coordinate $\text{Ti}(\text{bv})$ must, therefore, sink below the surface and produce no STM signal, as reported from calculations.⁶ $-\text{Ti}(\text{bv})\text{O}_2-\text{O}$ shows the correct registry with $\text{Ti}(\text{bh})$ of the layer below.⁴ It is not clear whether distortion of O’s at the edge of the reconstruction is sufficient to match ion desorption results.^{6,5} This model may be extended to account for triple rows observed in STM,⁶ except insofar as the central row of the STM image seems to be displaced by $c/2$. A similar model is proposed in Ref. 22. A further model of this sort, in which TiO_2 stoichiometry is restored, is proposed for crosslinked (1×2) : $-\text{Ti}(\text{bv})\text{O}_2$.¹¹ Our previous calculations on stoichiometric (110) showed this reconstruction to be 0.26 J m^{-2} less stable than the unreconstructed surface.²⁶

II. COMPUTATIONAL METHOD

A. First-principles slab calculations

To describe the different Ti:3d electronic states of stoichiometric and reduced surfaces, an *ab initio* quantum chemical method is necessary: here self-consistent density functional theory is used. We impose three-dimensional (3D) periodic boundary conditions and so employ pseudopotentials and a plane wave basis for the ground-state electronic wave function. This “first-principles” method gives reliable predictions of structures, properties, and dynamics of periodic systems, while still viable in terms of computer power and execution time.³⁸ We use the VIENNA AB INITIO SIMULATION PACKAGE (VASP).^{39–41} The surface is modeled by an infinite series of stacked “slabs” separated by vacuum.

A reliable but efficient set of technical parameters for the first-principles calculations was established in our previous study on the stoichiometric rutile surface²⁶ and we use the same parameters here, as follows. The gradient-corrected density functional of Perdew *et al.* is employed⁴² along with the appropriate ultrasoft pseudopotentials supplied with VASP (Ref. 43)—O:six-electron $2s2p$ (He core) and Ti:four-electron $4s3d$ (Ar core). Spot checks indicate that, even in reduced systems, explicit inclusion of Ti:3p electrons affect ΔE by only 0.1 eV (Table I). Reciprocal space is spanned by a plane wave basis up to 396 eV with Monkhorst-Pack k -point sampling.⁴⁴ out of computational necessity we use just one k point in the irreducible Brillouin zone for (1×2) slabs ($k_x \times k_y \times k_z = 2 \times 1 \times 1$). The test results in Table I show that absolute energies are adequately converged with respect to basis size but not with respect to k points: a finer sampling than we employ may alter relative energetics of reduced slabs by as much as 0.2 eV. Self-consistent steps are converged to 10^{-4} eV and slab geometry is optimized under no symmetry restraints with no fixed atoms to gradients

TABLE I. Variation of absolute first-principles energy (eV) with technical parameters of selected $+4.5\text{Å}$ (Ref. 26) and $+4.5\text{Å}/\square_{\text{O}}$ slabs. The relative energy of the less stable isomer is also given for each method (in parentheses, eV). The standard parameters are used for all calculations except as detailed in the first column.

Method	Stoichiometric		Reduced	
	$[\text{Ti}(\text{iv})\text{O}_2]_2$	$+\text{Ti}(\text{bh})_2\text{O}_4, \text{O} \rightarrow \text{O}'$	$+\text{Ti}(\text{iv})_2\text{O}_3$	$+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{O}_3$
Standard ^a	−481.284	−481.088, (0.20)	−473.345	−472.316, (1.03)
basis ≤ 495 eV	−481.141	−480.954, (0.19)	−473.219	−472.180, (1.04)
$4 \times 2 \times 1$ k -points	−478.966	−479.078, (−0.11)	−471.679	−470.823, (0.86)
$\text{Ti}:3p^6 4s^2 3d^2$	−486.107	−486.020, (0.09)	−477.913	−476.924, (0.99)
Relaxed spin			−473.359	−472.325, (1.03)

^aPlane wave basis cutoff of 396 eV, $2 \times 1 \times 1$ k points, explicit $\text{Ti}:4s^2 3d^2$ electrons and fixed triplet spin for reduced systems (see Sec. II A).

$< 10^{-3}$ eV/Å. All energy differences ΔE are between optimized systems with no correction for zero-point energy.

There is one significant change in our method. By creating one neutral O vacancy per (1×2) unit cell (denoted $\square_{\text{O}}$), two extra electrons are added to the cell and these occupy states at the lower edge of the conduction band. (The slabs are not symmetric: only one face is reconstructed and reduced. Unlike STM experiments, where bulk rutile is reduced, the interior of our model slabs remain stoichiometric). We have chosen to align the electrons with fixed parallel spin and compute neutral triplet slabs in spin-polarized density-functional theory. Brief checks that allow the spin state to relax (towards the alternative singlet) have little effect on geometry and energetics (Table I). Note that we designate slabs as “ $\square_{\text{O}}$ reduced” merely to quantify the degree of nonstoichiometry and not to indicate a structural vacancy at an O site.

The fixed cell dimensions used for the slab are those optimized for the bulk in our earlier study ($a=4.640$ Å, $c/a=0.6411$, and $u=0.3071$,²⁶ agreeing with experiment within 1%).⁴⁵ Because there are even more possible reduced reconstructions than stoichiometric ones, it is necessary to limit computational effort to an appropriate level of accuracy. Earlier work indicated that thin 2Å slabs showed qualitatively correct structures but that the corresponding energetics could be in error by 1 eV per slab. More realistic 4Å and 6Å slabs gave quantitative agreement for ΔE (< 0.4 eV).²⁶ Thus in this study, ΔE from $2\text{Å}/\square_{\text{O}}$ calculations are used to screen out the 25 least likely structures. All remaining isomers are calculated at the $4\text{Å}/\square_{\text{O}}$ level, with only the 23 most stable being refined at $6\text{Å}/\square_{\text{O}}$. As in Ref. 26, slabs are separated by a vacuum of $z=16.4$ Å (5Å).

B. Survey of isomers

We seek to survey as many isomers of surface reconstructions as possible and order them according to relative stability. To this end a wide range of start geometries was generated in a pseudocombinatorial fashion by systematically arranging ions at all possible sites on one face of the slab, based on electrostatic arguments, optimized stoichiometric structures,²⁶ and the bonding patterns emerging in reduced systems. We consider slabs that are singly reconstructed and $\square_{\text{O}}$ reduced on the top face: the bottom face is an unrecon-

structed, stoichiometric bulk termination. These singly-reconstructed slabs are grouped into four classes by chemical formula: $\pm 0\text{Å}/\square_{\text{O}}$, $+0.25\text{Å}/\square_{\text{O}}$, $+0.5\text{Å}/\square_{\text{O}}$, $-0.25\text{Å}/\square_{\text{O}}$, as explained in Sec. I C. One hundred local minima were screened as described above (Sec. II A): of these, 57 show $\Delta E_{\text{surf}} \leq 2.0$ eV. We are limited by space to presenting here only the 40 most significant of these low-energy isomers; the rest are to be found along with the less stable isomers ($\Delta E_{\text{surf}} > 2.0$ eV) in supplementary information.⁴⁶ Of course, it is unlikely that we have discovered *all* the minimum-energy structures and some of our minima may be artifacts of the (1×2) symmetry imposed on the system.

C. Calculating surface energies

It is possible to compare two surfaces of different composition via their surface energies (E_{surf}): the lower this energy, the more stable the surface. For a stoichiometric $(\text{Ti}_4\text{O}_8)_{N_i}$ slab, E_{surf} can be calculated by partitioning the absolute first-principles energy E_i into bulk and surface contributions,

$$E_i = N_i E_{\text{bulk}} + E_{\text{surf}}, \quad (1)$$

where E_{surf} is the sum of surface energies for top and bottom slab faces. For the reduced slabs of this study, from which one O atom has been abstracted, we correct E_{surf} by the absolute energy of an isolated O atom.⁶¹

$$E_i + E(\text{O}) = N_i E_{\text{bulk}} + E_{\text{surf}}. \quad (2)$$

If a straight line is fitted to $E_i + E(\text{O})$ vs N_i , Eq. (2) means that E_{bulk} is the slope of this line and E_{surf} the intercept at $N=0$. This value of E_{surf} is thus very sensitive to small differences in the fit for E_{bulk} . As shown in Refs. 47–50, even small discrepancies in E_{bulk} will accumulate with N_i and cause E_{surf} to diverge and so it is preferable to find both E_{bulk} and E_{surf} from slab calculations only. In an earlier investigation of this problem we fitted to data from 5Å to 8Å unreconstructed stoichiometric slabs to obtain $E_{\text{bulk}}(u) = -107.833$ eV per (1×2) 1Å Ti_4O_8 unit.²⁶ Assuming that the bulk layers at the center of a reduced slab behave like stoichiometric layers, we use this value for E_{bulk} in the current study as well. Energetic effects due to nonstoichiometry will, therefore, be reflected in E_{surf} . E_{surf} is then fitted to

calculated E_i for the largest reduced slabs via Eq. (2). Figure 7 shows fits to E_{surf} for four low-energy isomers, one from each of the classes $\pm 0/\square_{\text{O}}$, $+0.25/\square_{\text{O}}$, $+0.5/\square_{\text{O}}$, $-0.25/\square_{\text{O}}$. Our experience in earlier work²⁶ shows that fitting to E_i from slabs of thickness $N \geq 5$ is sufficient for ± 0.1 eV accuracy. Therefore, E_{surf} is in fact simply obtained by averaging the two $[E_i + E(\text{O}) - NE_{\text{bulk}}]$ values for $N = 5, 6$. In this paper, E_{surf} is generally quoted in eV per (1×2) cell relative to the most stable reduced reconstruction. The absolute value of E_{surf} is of limited accuracy and not directly of interest.²⁶

III. RESULTS

A. Overview of energetics

Reduced reconstructions were generated as described in Sec. II B. Optimized geometries are shown in Figs. 3–6 and relative energies in Tables II–V. All energy differences ΔE in each class are between optimized systems with the same cell size and number of atoms, and are quoted in eV per (1×2) cell. The energetic data presented in the following sections are always those from the thickest available slab.

Energetics across these classes are obtained by the calculation of surface energy (Sec. II C). Figure 7 illustrates the fitting for four low-energy reconstructions, one from each class. The results are

$$\pm 0/\square_{\text{O}} r = -\text{O}, \text{O} \rightarrow \text{O}': E_{\text{surf}}(r) + E_{\text{surf}}(u) = 10.9 \pm 0.1 \text{ eV},$$

$$+0.25/\square_{\text{O}} r = +\text{Ti}(\text{iv})\text{O}_2 - \text{O}: E_{\text{surf}}(r) + E_{\text{surf}}(u) = 11.0 \pm 0.1 \text{ eV},$$

$$+0.5/\square_{\text{O}} r = +\text{Ti}(\text{iv})_2\text{O}_3: E_{\text{surf}}(r) + E_{\text{surf}}(u) = 10.0 \pm 0.1 \text{ eV},$$

$$-0.25/\square_{\text{O}} r = [+ \text{Ti}(\text{iv})\text{O}_2]_2 \text{Ti}(\text{iv})\text{O}: E_{\text{surf}}(r) + E_{\text{surf}}(u) = 10.7 \pm 0.1 \text{ eV},$$

[$\text{O} \rightarrow \text{O}'$ denotes an anion moved to a nonbulk position; here, an in-plane oxide shares x coordinate with $\text{Ti}(\text{bh})$, rather than with $\text{Ti}(\text{bv})$]. Because the slabs are reconstructed (r) on one face and unreconstructed (u) on the other face, we use $E_{\text{surf}}(u) = 2.0 \pm 0.1$ eV from our previous work.²⁶ Thus, for the most stable reconstruction $r = +\text{Ti}(\text{iv})_2\text{O}_3$, $E_{\text{surf}}(r) = 8.0 \pm 0.2$ eV per (1×2) surface cell or $E_{\text{surf}}(r) = 3.29 \pm 0.08$ J m⁻². This is the datum against which relative surface energies are quoted in this work: $\Delta E_{\text{surf}}[\text{Ti}(\text{iv})_2\text{O}_3] = 0.0$ eV.

We combine isomer ΔE within classes and ΔE_{surf} across the classes to obtain the relative surface energies for every reconstruction listed in Tables II–V. As these are relative energies, independent of $E_{\text{surf}}(u)$, the estimated accuracy is that due to fitting (± 0.1 eV, Fig. 7).²⁶ The reconstructions computed to be of lowest surface energy are shown in Fig. 8. Top and side views in Fig. 9 highlight geometric details for selected isomers.

E_{surf} contains an adjustment for the computed energy of an O atom [Eq. (2)], but the reaction product of surface reduction is O_2 . E_{surf} can, therefore, be converted to a reduction energy by means of the dissociation energy $D_e(\text{O}_2) = 5.13$ eV.⁵¹ (This D_e is an experimental value; since electronic states are treated as single determinants, density-functional theory is inherently unsuited to calculating dissociation energies of this type, especially as the reaction is not isogyric).⁵² Subtraction of $D_e(\text{O}_2)/2$ from E_{surf} for $r = +\text{Ti}(\text{iv})_2\text{O}_3$ gives an approximate reduction energy of $\Delta E = 5.4$ eV per $\square_{\text{O}}$ (520 kJ mol⁻¹).

B. Added interstitial double row

The most stable reduced reconstruction found in this study is $+\text{Ti}(\text{iv})_2\text{O}_3$ [Fig. 5(a)], at least 0.3 J m⁻² lower in surface energy than other $\square_{\text{O}}$ -reduced reconstructions (Fig. 8).

$\text{Ti}(\text{iv})_2\text{O}_3$ is accommodated with little strain in the (110) layer beneath and the positions of ions in this layer closely resemble the unreconstructed stoichiometric surface. Thus $\text{Ti}(\text{bh})$ under the reconstruction relaxes 0.10 Å into the surface (compare 0.15 Å for the unreconstructed surface) and becomes almost five coordinate. Both surface $\text{Ti}(\text{bh})$ are undistorted within their horizontal ribbons, so that ribbon angles remain 98° – 99° [Fig. 9(c)]. All O are within 0.2 Å of bulk positions, except for the contraction of surface-bridging O into the reconstruction (± 0.4 Å along $[1\bar{1}0]$). The only appreciable distortion in the $+\text{Ti}(\text{iv})_2\text{O}_3$ slab is of $\text{Ti}(\text{iv})$: the cations accept almost tetrahedral coordination in the upper portion of the vertically oriented interstice, similar to the $+\text{Ti}(\text{iv})\text{O}_2$ decoration on both reduced (Sec. III E) and stoichiometric surfaces.⁵³ $\text{Ti}(\text{iv})$ is thus about $z = 2.7$ Å above Ti of the main surface (bulk layer $z = 3.3$ Å) and a distance of 3.5 and 3.3 Å from surface $\text{Ti}(\text{bv})$ and $\text{Ti}(\text{bh})$, respectively.

Along $[1\bar{1}0]$ $\text{Ti}(\text{iv})_2\text{O}_3$ can be described as a pair of corner-sharing tetrahedra, with the $\text{Ti}(\text{iv})$ - $\text{Ti}(\text{iv})$ distance matching the optimum value computed for corner-sharing octahedra in the bulk [$\text{Ti}(\text{bv})$ - $\text{Ti}(\text{bh}) = 3.6$ Å]. Ti -O distances within the tetrahedron are 1.8 – 1.9 Å. We note that these geometric parameters match those optimized for the stoichiometric $+\text{Ti}(\text{iv})_2\text{O}_3 + \text{O}$ reconstruction²⁶ to ± 0.06 Å.

We find that the reduced surface is stabilized by 0.9 eV on reconstruction from the simplest isomer [$-\text{O}$, Fig. 3(b)] to $+\text{Ti}(\text{iv})_2\text{O}_3$. Similar stabilization is computed for $[-\text{Ti}(\text{bh})\text{O}_2 + \text{Ti}(\text{iv})_2\text{O}_3]$ [Fig. 4(a)]: the $-\text{Ti}(\text{bh})\text{O}_2 - \text{O}$ isomer is made 0.7 eV more stable by the bridge of $\text{Ti}(\text{iv})_2\text{O}_3$ across the gap. Likewise, $+\text{Ti}(\text{bv})\text{O}_2 + \text{Ti}(\text{iv})_2\text{O}_3$ [Fig. 6(h)] is stabilized by 1.0 eV relative to $+\text{Ti}(\text{bv})\text{O}_2 - \text{O}$.⁴⁶ Among the stoichiometric reconstructions of our earlier work, $+\text{Ti}(\text{iv})_2\text{O}_3 + \text{O}$ was about 1 eV more stable than comparable isomers.²⁶ It would appear that this is not due to any intrinsic stability of the $\text{Ti}(\text{iv})_2\text{O}_3$ structure, rather a result of favorable interaction between the completely bulk-terminated (110) sublayer and the reconstructed and polarized cations. Evidence for this comes from estimated E_{surf} for thin $\text{Ti}(\text{iv})_2\text{O}_3$ films: an isolated $+0.5/\square_{\text{O}}$ strand shows $E_{\text{surf}} = 10.5$ eV [Eq. (2)], but this drops to 10.3 , 9.7 , and 10.0 eV as bulk layers are added to form a slab ($N = 1.5, 2.5$, and 3.5 , respectively, in Fig. 7).

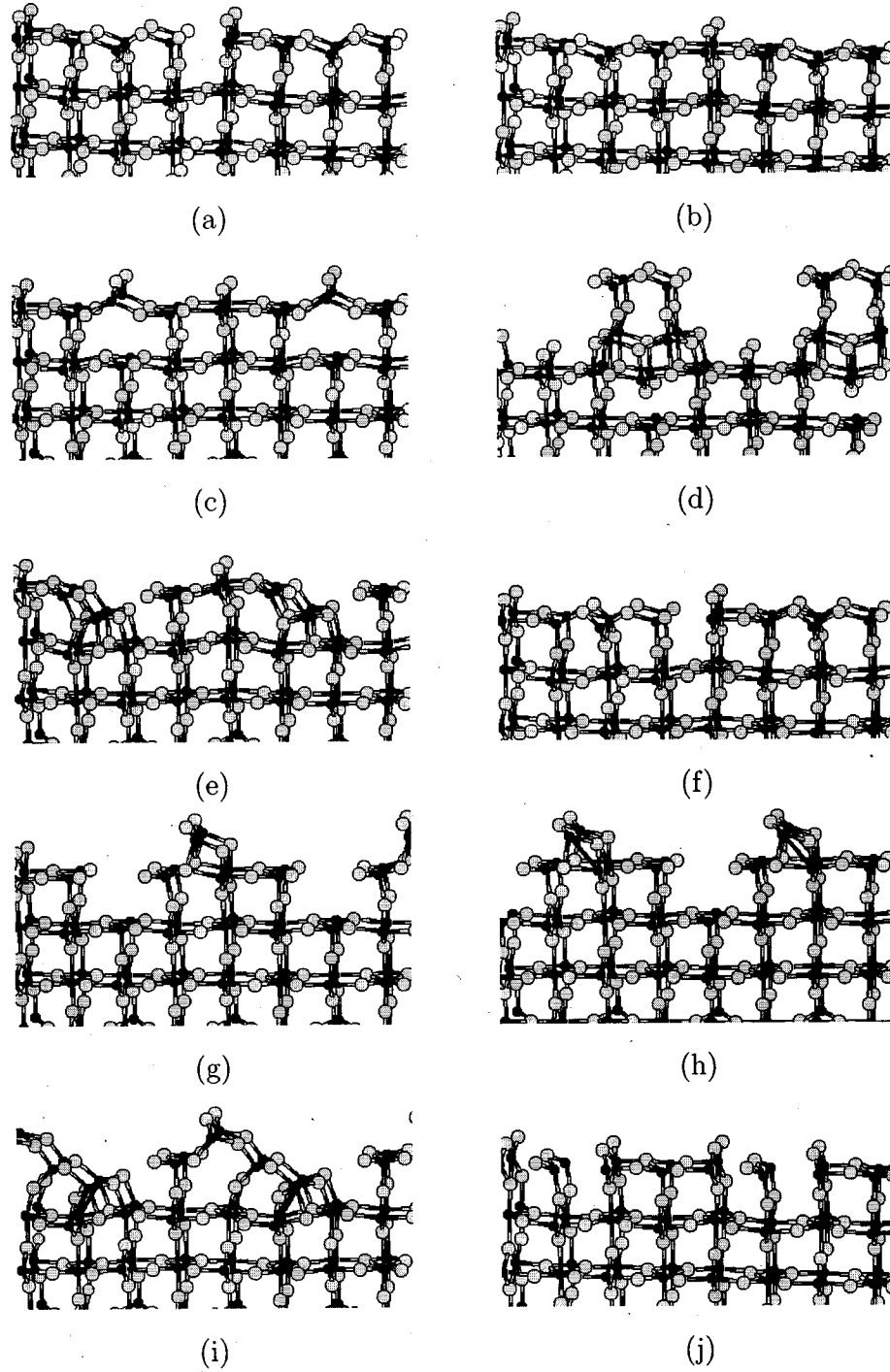


FIG. 3. Section of slab, expanded in x and y , showing computed reduced $\pm 0/\square_{\text{O}}$ surface reconstructions $\text{Ti}_{4\text{N}}\text{O}_{8\text{N}-1}$ as listed in Table II. (a) $-\text{O}, \text{O} \rightarrow \text{O}'$, (b) $-\text{O}$, (c) $-\text{O}_{\text{sub}}$, (d) $+\text{Ti}(\text{ih})_2[\text{Ti}_2]\text{O}_7$, (e) $-\text{Ti}(\text{bv})\text{O} + \text{Ti}(\text{ih})$, (f) $-\text{O}, (\text{O} \rightarrow \text{O}')$, (g) $-\text{Ti}(\text{bv})\text{O}_2 + \text{Ti}(\text{iv})\text{O}$, (h) $-\text{Ti}(\text{bv})\text{O}_2 + \text{Ti}(\text{ih})\text{O}$, (i) $+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{Ti}(\text{iv})\text{O}_6 + \text{Ti}(\text{ih})\text{O}$, (j) $-\text{O}_{\text{in plane}}$.

C. Reduction by removal of oxygen

The simplest models for the (1×2) reduced surface are obtained from the unreconstructed surface by removal of one O atom from every second cell and allowing the structure to relax. Of these reconstructions, removal of the supersurface O that bridges Ti(bv) [$-\text{O}$, Fig. 3(b)] gives the discounted “missing-row” model (Sec. 1 D).¹⁸ We calculate a surface

energy of 0.9 ± 0.1 eV per (1×2) cell relative to the $\text{Ti}(\text{iv})_2\text{O}_3$ reconstruction, which agrees with the result of 0.95 eV from thin $3/\square_{\text{O}}$ slabs.²⁷ Isoenergetic at this level of accuracy is an isomer with anions at nonbulk sites [denoted O' ; Fig. 3(a)]. A structure missing the subsurface bridging O is only 0.2 eV less stable [Fig. 3(c)]. By contrast, removal of an in-plane O is much less favored, at $\Delta E_{\text{surf}} = 2.0$ eV [Fig. 3(j)].

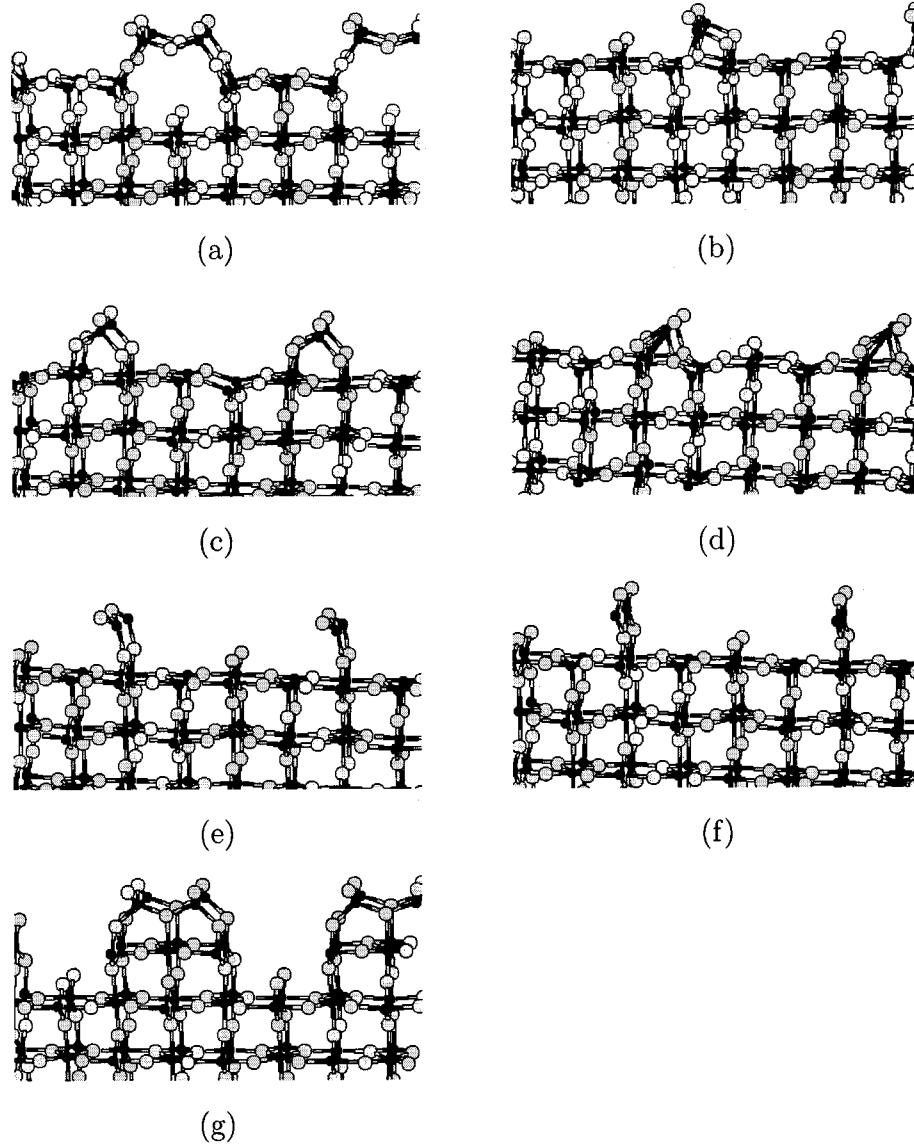


FIG. 4. Section of slab, expanded in x and y , showing computed reduced $+0.25/\square_{\text{O}}$ surface reconstructions $(\text{Ti}_4\text{O}_8)_N\text{TiO}$ as listed in Table III. (a) $-\text{Ti}(\text{bh})\text{O}_2 + \text{Ti}(\text{iv})_2\text{O}_3$, (b) $+\text{Ti}(\text{iv})\text{O}$, (c) $+\text{Ti}(\text{iv})\text{O}_2-\text{O}$, (d) $+\text{Ti}(\text{ih})\text{O}$, (e) $+\text{Ti}(\text{bh})\text{O}$, (f) $+\text{Ti}(\text{bh})\text{O}$, (g) $+\text{Ti}(\text{bv})\text{Ti}(\text{bh})-\text{Ti}(\text{bv})\text{O}_6 + \text{Ti}(\text{iv})_2\text{O}_3$.

It is instructive to analyze the optimized geometry of the simple $-\text{O}$ surface [Fig. 3(b)]. The undercoordinated $\text{Ti}(\text{bv})$ cation relaxes $z=0.4$ Å into the surface and neighboring in-plane O's contract towards it to give $\text{Ti}(\text{bv})-\text{O}$ of 1.93 Å [compare computed bulk Ti-O of 2.01 and 1.95 Å (axial and equatorial)]. Fourfold coordination is thus restored to $\text{Ti}(\text{bv})$, in an almost tetrahedral arrangement. As a consequence, however, neighboring horizontal rutile ribbons are distorted to give $\text{Ti}-\text{O}-\text{Ti}$ angles of 91° , as illustrated in the top view of this surface in Fig. 9(a). These strained ribbons occur in other reduced reconstructions (Secs. III D and IV C).

D. Reduction by addition of TiO

While the notation TiO_{2-x} and $\square_{\text{O}}$ implies oxygen deficiency, in this section we take the alternative

viewpoint, namely, reduction by addition of a neutral TiO unit.

The simplest reconstructions of this type are in the class $+0.25/\square_{\text{O}}$: $+\text{Ti}(\text{iv})\text{O}$ or $+\text{Ti}(\text{ih})\text{O}$. [Table III, Figs. 4(b) and 4(d)]. The bulklike $+\text{Ti}(\text{bh})\text{O}$ [Fig. 4(e)] is less stable by only 0.4–0.5 eV: for comparison, the corresponding stoichiometric reconstructions were found to be 1–2 eV less stable.²⁶ Addition of TiO at interstitial surface sites is also reported in first-principles calculations on reduced reconstructed (1×3) TiO_2 (100).⁵⁷ This trend for the reduced surface continues into the $+0.5/\square_{\text{O}}$ class (Table IV), where all of the mixed bulk-interstitial isomers $+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{O}_3$, $+\text{Ti}(\text{bv})\text{Ti}(\text{ih})\text{O}_3$, and $+\text{Ti}(\text{bv})\text{Ti}(\text{iv})\text{O}_3$ [Figs. 5(b, c, and g)] show $\Delta E_{\text{surf}}=1.1$ eV, and are thus 0.3–0.7 eV more stable than the bulk-terminated variants $+\text{Ti}(\text{bh})_2\text{O}_4-\text{O}$, $+\text{Ti}(\text{bh})\text{Ti}(\text{bv})\text{O}_3$, $\text{O} \rightarrow \text{O}'$, $+\text{Ti}(\text{bh})\text{Ti}(\text{bv})\text{O}_4-\text{O}$ and

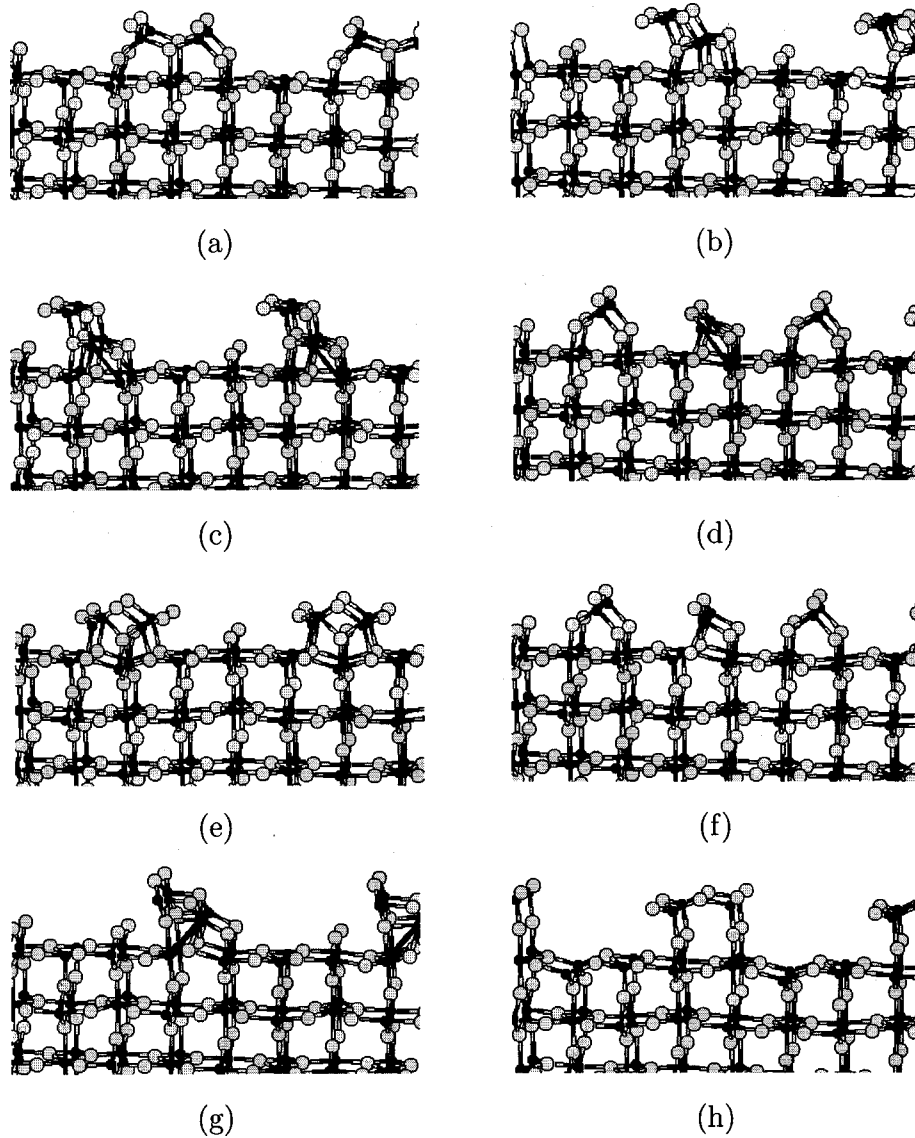


FIG. 5. Section of slab, expanded in x and y , showing (a)–(m) the optimized geometries of reduced $+0.5/\square_{\text{O}}$ surface reconstructions $(\text{Ti}_4\text{O}_8)_N\text{Ti}_2\text{O}_3$ as listed in Table IV. (a) $+\text{Ti}(\text{iv})_2\text{O}_3$, (b) $+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{O}_3$, (c) $+\text{Ti}(\text{bv})\text{Ti}(\text{ih})\text{O}_3$, (d) $+\text{Ti}(\text{ih})\text{O}+\text{Ti}(\text{iv})\text{O}_2$, (e) $+\text{Ti}(\text{iv})\text{O}+\text{Ti}(\text{iv})\text{O}_2$, (f) $+\text{Ti}(\text{ih})_2\text{O}_3$, (g) $+\text{Ti}(\text{bv})\text{Ti}(\text{iv})\text{O}_3$, (h) $+\text{Ti}(\text{bh})_2\text{O}_4-\text{O}$, (i) $+\text{Ti}(\text{bh})\text{Ti}(\text{bv})\text{O}_3$, $\text{O} \rightarrow \text{O}'$, (j) $+\text{Ti}(\text{ih})\text{Ti}(\text{iv})\text{O}_3$, (k) $+\text{Ti}(\text{bh})\text{Ti}(\text{bv})\text{O}_4-\text{O}$, (l) $+\text{Ti}(\text{ih})[\text{Ti}]\text{O}_3$, (m) $+\text{Ti}(\text{bh})\text{Ti}(\text{bv})\text{O}_3$. (n) $+\text{Ti}(\text{ih})_2\text{O}_3$ is an unstable structure, which on optimization gives (a).

$+\text{Ti}(\text{bh})\text{Ti}(\text{bv})\text{O}_3$ [Figs. 5(h, i, k and m)]. However for $-0.25/\square_{\text{O}}$ and $\pm 0/\square_{\text{O}}$, as in the stoichiometric case,²⁶ the oxide sub-lattice of an almost complete layer favors cations in bulk rather than interstitial sites. Thus, addition to the $-\text{Ti}(\text{bv})\text{O}_2-\text{O}$ isomer [Fig. 6(d)] of $\text{Ti}(\text{iv})\text{O}$ or $\text{Ti}(\text{ih})\text{O}$ [Figs. 3(e, g, and h)] costs 0.4–0.8 eV. No low-energy reconstructions could be found with a complete layer of four interstitial Ti. Focusing, therefore, on examples of the interstitial $+0.25/\square_{\text{O}}$ and mixed bulk-interstitial $+0.5/\square_{\text{O}}$ reconstructions, we present detailed results for $+\text{Ti}(\text{ih})\text{O}$ and $+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{O}_3$.

The surface energy of the $+\text{Ti}(\text{ih})\text{O}$ reconstruction [Fig. 4(d)] is computed to be 1.0 ± 0.1 eV, isoenergetic with the $-\text{O}$ reduced surface (Sec. III C). $\text{Ti}(\text{ih})\text{O}_2$ ribbons stack almost horizontally on top of the $\text{Ti}(\text{bh})\text{O}_2$ ribbons of the

surface, displaced by half a cell in $x=[001]$ and a quarter of a cell in $y=[110]$. Relative to the ions of the surface layer, $\text{Ti}(\text{ih})$ is 2.0 Å above the axial in-plane O and 2.7 and 3.4 Å from $\text{Ti}(\text{bv})$ and $\text{Ti}(\text{bh})$, respectively. (In the bulk, distances from Ti to the centers of interstices are computed to be 2.4 and 2.7 Å.) Top and side views are shown in Fig. 9(d). In the top view $+\text{Ti}(\text{ih})\text{O}$ may be seen to distort the oxide anions of the underlying layer in a way similar to the $-\text{O}$ surface [Fig. 9(a)], reducing Ti-O-Ti angles of horizontal rutile ribbons from 100° to approximately 90° on one side. We note that similar distortion was observed to accompany the rather unstable stoichiometric reconstruction $+\text{Ti}(\text{ih})\text{O}_2$.²⁶ The horizontal ribbons of the $+\text{Ti}(\text{ih})\text{O}$ reconstruction itself form 90° angles where constrained by the connection to the surface $\text{Ti}(\text{bv})$. The side view shows that

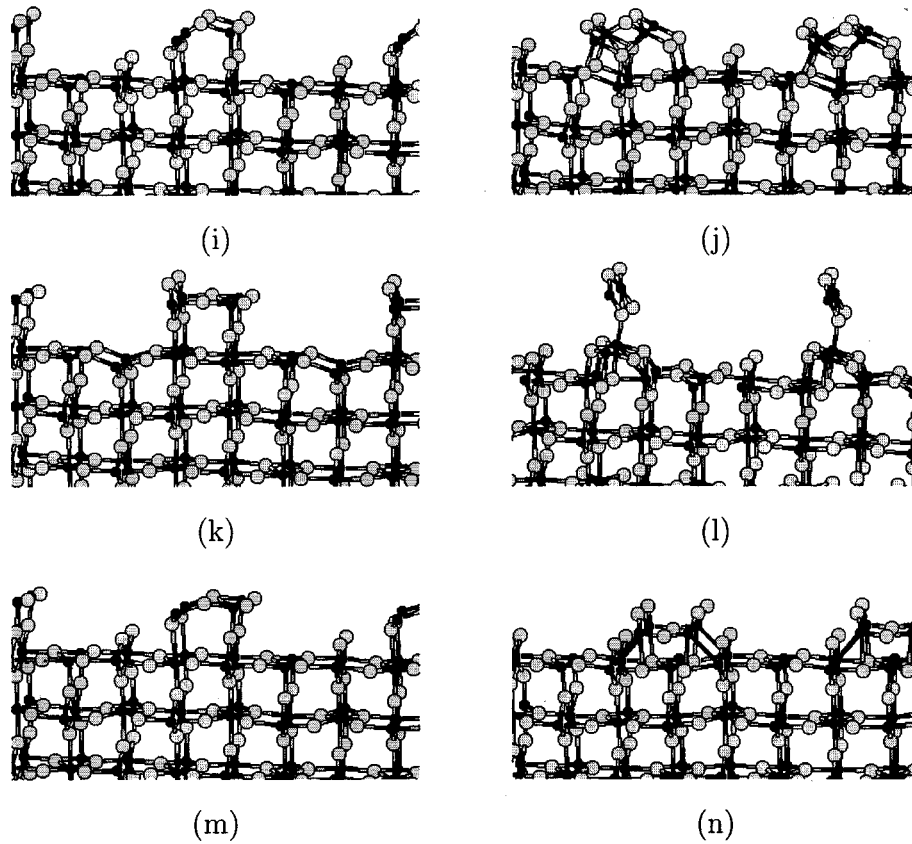


FIG. 5. (Continued.)

the vertical ribbons of these $\text{Ti}(\text{bv})\text{O}_2$ are also distorted to near 90° .

The picture is essentially the same in the more complex mixed reconstruction $+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{O}_3$ [Fig. 5(b)]. The top-most $\text{Ti}(\text{bh})\text{O}_2$ ribbons stack on top of the $\text{Ti}(\text{ih})\text{O}_2$ ribbons in just the same way as detailed above for $\text{Ti}(\text{ih})\text{O}_2$ relative to the surface. $\text{Ti}(\text{bh})$ of the reconstruction is $2.0 \text{ \AA}$ above axial O and $3.0 \text{ \AA}$ from $\text{Ti}(\text{ih})$. Meanwhile, $\text{Ti}(\text{ih})$ relaxes to 3.0 and $3.2 \text{ \AA}$ from the surface $\text{Ti}(\text{bv})$ and $\text{Ti}(\text{bh})$. The top view in Fig. 9(e) shows the same pattern of distortion of horizontal ribbons to about 90° on one side. On the other hand, strain in vertical ribbons has been relieved (side view).

As noted above, reconstructions obtained by addition to the other interstitial site [$+\text{Ti}(\text{iv})\text{O}$, Fig. 4(b)] or to other bulk sites [$+\text{Ti}(\text{bv})\text{Ti}(\text{ih})\text{O}_3$ and $+\text{Ti}(\text{bv})\text{Ti}(\text{iv})\text{O}_3$, Figs. 5(c) and (g)] also show $\Delta E_{\text{surf}} = 1.1 \pm 0.1 \text{ eV}$. The optimized geometries show the same pattern of short Ti-Ti and distorted-ribbon angles. Just one example is given in Fig. 9(f): $+\text{Ti}(\text{bv})\text{Ti}(\text{iv})\text{O}_3$. Here, vertical rather than horizontal ribbons of the reconstruction are distorted to accommodate the interstitial and $\text{Ti}(\text{iv})$ shows distances of 3.0 , 3.2 , and $2.9 \text{ \AA}$ to reconstructed $\text{Ti}(\text{bv})$, surface $\text{Ti}(\text{bv})$, and surface $\text{Ti}(\text{bh})$, respectively. However, distortion of vertically oriented ribbons is a less reliable indicator of strain, as it is the nature of the slab model to allow vertical displacement of ions. A further caveat is that the strain noted above may merely be the result of the fixed cell dimensions and (1×2) periodicity of our calculations.

E. Stoichiometric decoration at interstitial rows

In our earlier work on stoichiometric reconstructions, we consistently found that sections of bulk-terminated (110) could be decorated along the $[001]$ interstitial channels, a reconstruction termed $+\text{Ti}(\text{iv})\text{O}_2$. The energetic cost was very slight: $0.1 \pm 0.1 \text{ eV}$ per TiO_2 or $0.04 \pm 0.04 \text{ J m}^{-2}$.⁵³ The current work is concerned with reduced surfaces and the occurrence of reduced units at interstitial sites such as $\text{Ti}(\text{iv})\text{O}$ and $\text{Ti}(\text{ih})\text{O}$ is discussed in Sec. III D. However, the stoichiometric decoration $+\text{Ti}(\text{iv})\text{O}_2$ is observed with the same ubiquity as in the earlier work.

Thus, the simple “missing-row” reconstruction [$-\text{O}$, Fig. 3(b)] can be decorated to give $+\text{Ti}(\text{iv})\text{O}_2-\text{O}$ [Fig. 4(c)] at a surface energy cost of just 0.2 eV per (1×2) cell. Likewise, while $+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{O}_3$ and $+\text{Ti}(\text{bv})\text{Ti}(\text{iv})\text{O}_3$ [Figs. 5(b) and (g)] show ΔE_{surf} of $1.1 \pm 0.1 \text{ eV}$, ΔE_{surf} is raised only slightly to 1.2 – 1.3 eV by the addition of adjacent $\text{Ti}(\text{iv})\text{O}_2$ rows [Figs. 6(e) and (g)] or $+\text{Ti}(\text{iv})\text{O}_2$ on top [Fig. 6(f)]. More complicated surface reconstructions are possible, based on multiple decorations. Starting from $+\text{Ti}(\text{iv})\text{O}$ [Fig. 4(b)], repeated addition of $\text{Ti}(\text{iv})\text{O}_2$ changes the surface energy by $+0.1 \text{ eV}$ and then -0.4 eV [Figs. 5(e) and 6(a)]. More strikingly, the reconstructions obtained by decorating the $+\text{Ti}(\text{ih})\text{O}$ isomer are isoenergetic at our level of accuracy: $\Delta E_{\text{surf}} = 1.1 \pm 0.1 \text{ eV}$ [Figs. 4(d), 5(e), and 6(c)]. An exceptional case is the 1.1 eV stabilization of the surface that we compute for the addition of $\text{Ti}(\text{iv})\text{O}_2$ to $+\text{Ti}(\text{iv})\text{O}$ to give $+\text{Ti}(\text{iv})_2\text{O}_3$, but this reconstruction merits separate consideration (Sec. III B).

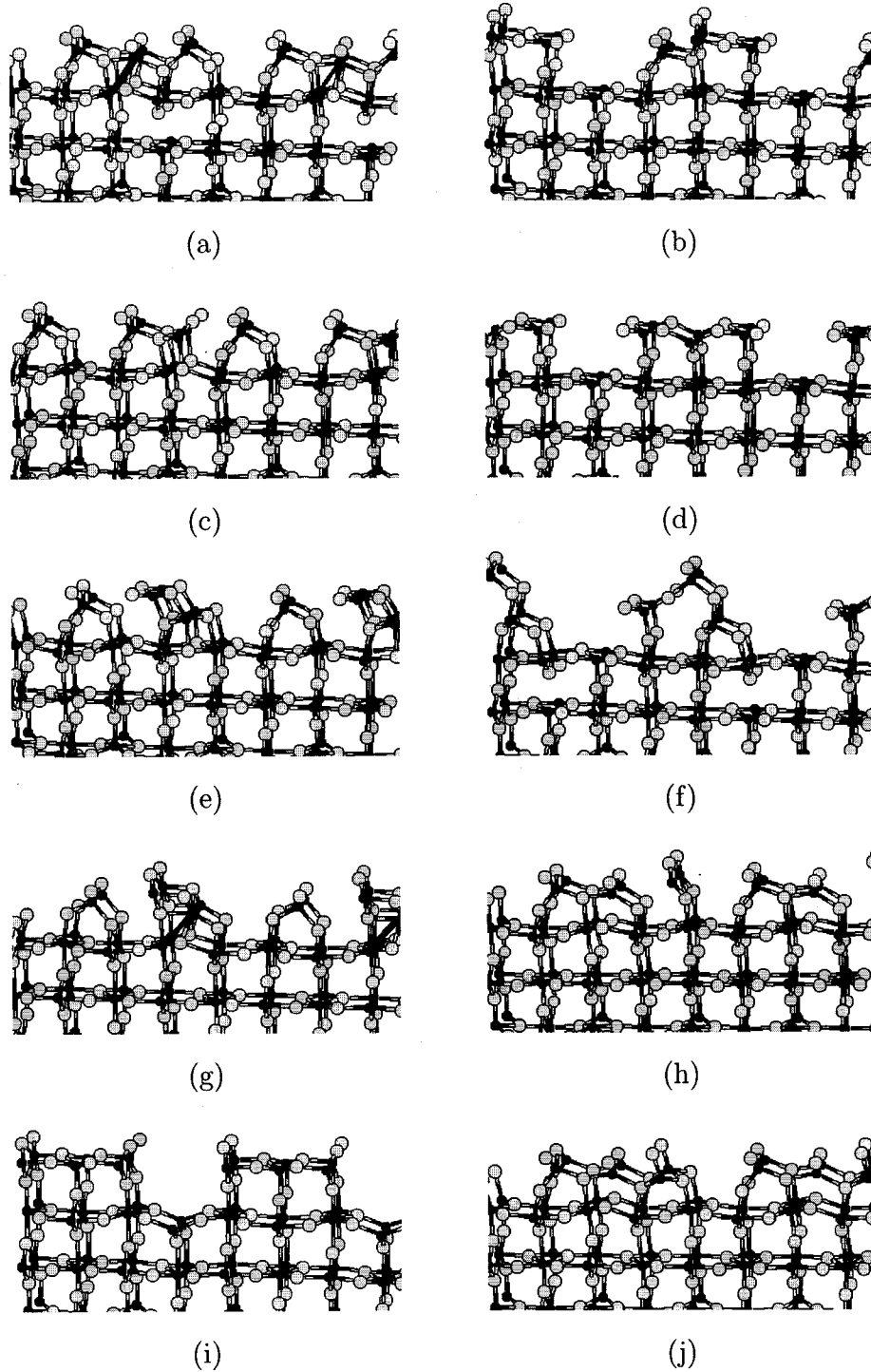


FIG. 6. Section of slab, expanded in x and y , showing computed reduced $-0.25/\square_{\text{O}}$ surface reconstructions $(\text{Ti}_4\text{O}_8)_N\text{Ti}_3\text{O}_5$ as listed in Table V. (a) $[\text{+Ti(iv)O}_2]_2\text{Ti(iv)O}$, (b) $+\text{Ti(iv)Ti(bv)Ti(bh)O}_5$, (c) $[\text{+Ti(iv)O}_2]_2\cdot\text{Ti(ih)O}$, (d) $-\text{Ti(bv)O}_2-\text{O}$, (e) $+\text{Ti(bh)Ti(ih)O}_3+\text{Ti(iv)O}_2$, (f) $+\text{Ti(bh)[Ti(iv)]Ti(ih)O}_5$, (g) $+\text{Ti(bv)Ti(iv)O}_3+\text{Ti(iv)O}_2$, (h) $+\text{Ti(iv)}_2\text{O}_3+\text{Ti(bv)O}_2$, (i) $-\text{Ti(bh)O}_2-\text{O}$, (j) $+\text{Ti(iv)}_2\text{O}_3\cdot\text{Ti(ih)O}_2$.

From a technical point of view, these results validate our estimate of relative surface energies (Sec. II C, Fig. 7) across all classes of reconstruction ($\pm 0/\square_{\text{O}}$, $+0.25/\square_{\text{O}}$, etc.). More importantly, we conclude that rows of interstitial decorations are a general feature of rutile surfaces, stoichiometric, and reduced. Possible reasons for these energetics are advanced in Sec. IV C.

IV. DISCUSSION

A. Assigning the (1×2) reconstruction

Considering solely the first-principles energetic data presented here, it is clear that the $(1\times 2)\square_{\text{O}}$ -reduced reconstruction may be assigned to $+\text{Ti(iv)}_2\text{O}_3$ [Fig. 5(a), Sec. III B]. We have found no other reduced reconstruction that is

TABLE II. Energies of $\pm 0/\square_{\text{O}}$ singly reconstructed reduced N -layer (1×2) slabs of the formula $\text{Ti}_{4N}\text{O}_{8N-1}$ relative to the lowest-energy reduced reconstruction of this type “ $-\text{O}_2\text{O} \rightarrow \text{O}'$ ” (absolute first-principles $E = -203.753$ eV, -418.693 eV, -634.142 eV for $N=2, 4, 6$). ΔE_{surf} per (1×2) cell are ± 0.1 eV and are relative to $+\text{Ti}(\text{iv})_2\text{O}_3$. Data are given for $\Delta E_{\text{surf}} \leq 2.0$ eV; higher-energy reconstructions are in supplementary information (Ref. 46). $\text{O} \rightarrow \text{O}'$ indicates anions at nonbulk sites.

Reconstruction $\pm 0/\square_{\text{O}}$	ΔE (eV)			$\Delta E_{\text{surf}}(r)$ (eV)	Fig.
	$2/\square_{\text{O}}$	$4/\square_{\text{O}}$	$6/\square_{\text{O}}$		
$-\text{O}_2\text{O} \rightarrow \text{O}'$	0.00	0.00	0.000	0.9	3(a)
$-\text{O}$	0.22	0.07	0.001	0.9	3(b)
$-\text{O}_{\text{sub}}$	0.82	0.29	0.17	1.1	3(c)
$+\text{Ti}(\text{ih})_2[\text{Ti}_2]\text{O}_7$		0.58	0.39	1.3	3(d)
$-\text{Ti}(\text{bv})\text{O} + \text{Ti}(\text{ih})$	0.69	0.68		1.6	3(e)
$-\text{O}_2(\text{O} \rightarrow \text{O}')_2$	0.64	0.73		1.6	3(f)
$-\text{Ti}(\text{bv})\text{O}_2 + \text{Ti}(\text{iv})\text{O}$	1.51	0.78		1.7	3(g)
$-\text{Ti}(\text{bv})\text{O}_2 + \text{Ti}(\text{ih})\text{O}$	1.63	0.89		1.8	3(h)
$+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{Ti}(\text{iv})\text{O}_6 + \text{Ti}(\text{ih})\text{O}$	0.75	0.97		1.9	3(i)
$-\text{O}_{\text{in plane}}$	1.06	1.17		2.0	3(j)
Total cell z (Å)	22.96	29.52	36.08		

energetically competitive. $+\text{Ti}(\text{iv})_2\text{O}_3$ plausibly fits all experimental observations (Sec. I D).

As stated in Sec. III C, the missing-row model [Fig. 3(b)] shows a computed surface energy of 0.9 ± 0.1 eV per (1×2) cell or 0.4 ± 0.04 J m $^{-2}$ relative to the $\text{Ti}(\text{iv})_2\text{O}_3$ reconstruction. The proposed “added Ti_3O_5 row” reconstruction, which we denote $-\text{Ti}(\text{bv})\text{O}_2 - \text{O}$ [Fig. 6(d)] is 1.2 ± 0.1 eV or 0.5 ± 0.04 J m $^{-2}$ higher in surface energy than $+\text{Ti}(\text{iv})_2\text{O}_3$. Although unusually stable for a reconstruction featuring Ti at bulk-terminated sites only, this reconstruction is not energetically competitive. Rearrangement of one Ti to the unsymmetrical $+\text{Ti}(\text{iv})\text{Ti}(\text{bv})\text{Ti}(\text{bh})\text{O}_5$ isomer [Fig. 6(b)] is computed to be thermodynamically favored by 0.3 eV. Relaxation to a symmetrical $+\text{Ti}(\text{iv})\text{Ti}(\text{bv})\text{Ti}(\text{iv})\text{O}_4$ as postulated in Ref. 6 would only proceed with further reduction.

Figure 8 shows that there are many other (1×2) reconstructions in the same energy range as the missing row and

“added Ti_3O_5 .” Of these, three are symmetric [$-\text{O}_{\text{sub}}$, Fig. 3(b); $-\text{Ti}(\text{bh})\text{O}_2 + \text{Ti}(\text{iv})_2\text{O}_3$, Fig. 4(a); $+\text{Ti}(\text{ih})_2\text{O}_3$, Fig. 5(f)] and the latter two exhibit double rows and off-normal oxide anions, fitting most experimental criteria. Should any of these reconstructions occur on reduced (110), we expect that they would convert on high-temperature annealing to the thermodynamically favored $+\text{Ti}(\text{iv})_2\text{O}_3$, with a 0.4 J m $^{-2}$ lowering in surface energy. However, there may be more than one (1×2) surface phase. Xu *et al.* report conversion of reduced (1×2) to a corrugated (1×1) surface under vacuum at high temperature.¹³ The (1×2) surface of Onishi and Iwasawa undergoes no such conversion.¹² Conversely, Bennett and co-workers observe cycles of oxidative growth of the cross-linked phase $(12 \times 2) \rightarrow (1 \times 1) \rightarrow (12 \times 2)$, but no such reaction with O_2 for noncrosslinked (1×2) .¹⁶

Definitive assignments of model structures to STM images is not possible without reliable simulation of these im-

TABLE III. Energies of $+0.25/\square_{\text{O}}$ singly reconstructed reduced N -layer (1×2) slabs of the formula $\text{Ti}_{4N+1}\text{O}_{8N+1}$ relative to the reduced reconstruction $+\text{Ti}(\text{iv})\text{O}_2 - \text{O}$, which is low in energy across all slab thicknesses (absolute first-principles $E = -229.668$, -445.271 , -660.905 for $N=2, 4, 6$). ΔE_{surf} per (1×2) cell are worked out for this isomer too, are to an accuracy of ± 0.1 eV and are relative to $+\text{Ti}(\text{iv})_2\text{O}_3$. Data are given for $\Delta E_{\text{surf}} \leq 2.0$ eV; higher-energy reconstructions are listed in Ref. 46.

Reconstruction $+0.25/\square_{\text{O}}$	ΔE (eV)			$\Delta E_{\text{surf}}(r)$ (eV)	Fig.
	$2.25/\square_{\text{O}}$	$4.25/\square_{\text{O}}$	$6.25/\square_{\text{O}}$		
$-\text{Ti}(\text{bh})\text{O}_2 + \text{Ti}(\text{iv})_2\text{O}_3$	0.89	0.06	-0.07	0.9	4(a)
$+\text{Ti}(\text{iv})\text{O}$	-0.84	-0.19	-0.02	1.0	4(b)
$+\text{Ti}(\text{iv})\text{O}_2 - \text{O}$	0.00	0.00	0.00	1.0	4(c)
$+\text{Ti}(\text{ih})\text{O}$	-0.87	-0.19	0.03	1.0	4(d)
$+\text{Ti}(\text{bh})\text{O}$	-0.20	0.43		1.4	4(e)
$+\text{Ti}(\text{bh})\text{O}'$	-0.14	0.47		1.5	4(f)
$+\text{Ti}(\text{bv})\text{Ti}(\text{bh})\text{Ti}(\text{bv})\text{O}_6 + \text{Ti}(\text{iv})_2\text{O}_3$	1.78	0.75	0.64	1.6	4(g)
Total cell z (Å)	22.96	29.52	36.08		

TABLE IV. Energies of $+0.5\text{TiO}_2$ singly reconstructed reduced N -layer (1×2) slabs of the formula $\text{Ti}_{4N+2}\text{O}_{8N+3}$ relative to the lowest-energy reduced reconstruction $+\text{Ti}(\text{iv})_2\text{O}_3$ (absolute first-principles $E = -257.945$ eV, -473.345 eV, -688.902 eV for $N=2, 4, 6$). ΔE_{surf} per (1×2) cell (± 0.1 eV) are also relative to this reconstruction. Data are given for $\Delta E_{\text{surf}} \leq 2.0$ eV; higher-energy reconstructions are listed in Ref. 46.

Reconstruction		ΔE (eV)		$\Delta E_{\text{surf}}(r)$	Fig.
+0.5 $\square_{\text{O}}$	2.5 $\square_{\text{O}}$	4.5 $\square_{\text{O}}$	6.5 $\square_{\text{O}}$	(eV)	
+Ti(iv) ₂ O ₃	0.00	0.00	0.00	0.0	5(a)
+Ti(bh)Ti(ih)O ₃	0.72	1.03	1.10	1.1	5(b)
+Ti(bv)Ti(ih)O ₃	0.73	1.03		1.1	5(c)
+Ti(ih)O+Ti(iv)O ₂	1.28	1.15	1.11	1.1	5(d)
+Ti(iv)O+Ti(iv)O ₂	1.33	1.17	1.11	1.1	5(e)
+Ti(ih) ₂ O ₃	0.76	1.06	1.11	1.1	5(f)
+Ti(bv)Ti(iv)O ₃	1.32	1.10	1.13	1.1	5(g)
+Ti(bh) ₂ O ₄ −O	1.64	1.44		1.4	5(h)
+Ti(bh)Ti(bv)O ₃ , O→O′	1.35	1.53		1.5	5(i)
+Ti(ih)Ti(iv)O ₃	2.05	1.65		1.7	5(j)
+Ti(bh)Ti(bv)O ₄ −O	1.85	1.67		1.7	5(k)
+Ti(ih)[Ti]O ₃	1.37	1.69		1.7	5(l)
+Ti(bh)Ti(bv)O ₃	1.69	1.98		2.0	5(m)
Total cell z (Å)	22.96	29.52	36.08		

ages from first-principles calculations and this is the subject of ongoing work (reference in preparation).

B. Dislocation from rutile to rocksalt

From an idealized point of view, oxides of titanium vary continuously with stoichiometry from the rocksalt-structured TiO , via the nonstoichiometric “Magnéli phases” $\text{Ti}_n\text{O}_{2n-1}$, to fully oxidized TiO_2 rutile.^{28,54} (In fact, the situation is complicated by distinct structures for Ti_2O_3 and Ti_3O_5 and by the range of imperfections in near- TiO phases). It is thus

natural to consider the nonstoichiometric surfaces of this study in terms of the structural extremes of rutile and rock-salt.

Considering rutile first, the structure is characterized by TiO_2 ribbons. At the surface we find that TiO half ribbons are a consistent feature of many low-energy reconstructions; examples include $+\text{Ti}(\text{iv})\text{O}_2$ and $+\text{Ti}(\text{iv})_2\text{O}_3$. While removal of O to form a half ribbon must cost energy, we find that half ribbons are intrinsically stable, even in the absence of a rutile slab ($N=0.25, 0.5$ in Fig. 7), which hints at Ti-O covalency along the ribbon. It is interesting to note the rela-

TABLE V. Energies of -0.25TiO_2 singly reconstructed reduced N -layer (1×2) slabs of the formula $\text{Ti}_{4N-1}\text{O}_{8N-3}$ relative to the lowest-energy reduced reconstruction of this type $[+\text{Ti}(\text{iv})\text{O}_2]_2\text{Ti}(\text{iv})\text{O}$ (absolute first-principles $E = -176.822$, -391.879 , -607.312 eV for $N=2, 4, 6$). Relative ΔE_{surf} per (1×2) cell are ± 0.1 eV and are relative to $+\text{Ti}(\text{iv})_2\text{O}_3$. Data are given for $\Delta E_{\text{surf}} \leq 2.0$ eV; higher-energy reconstructions are in Ref. 46.

Reconstruction	ΔE (eV)			$\Delta E_{\text{surf}}(r)$	Fig.
-0.25TiO_2	1.75TiO_2	3.75TiO_2	5.75TiO_2	(eV)	
$[+\text{Ti}(\text{iv})\text{O}_2]_2\text{Ti}(\text{iv})\text{O}$	0.00	0.00	0.00	0.7	6(a)
$+\text{Ti}(\text{iv})\text{Ti}(\text{bv})\text{Ti}(\text{bh})\text{O}_5$	1.11	0.39	0.21	0.9	6(b)
$[+\text{Ti}(\text{iv})\text{O}_2]_2\cdot\text{Ti}(\text{ih})\text{O}$	0.53	0.48	0.38	1.1	6(c)
$-\text{Ti}(\text{bv})\text{O}_2-\text{O}$	1.41	0.64	0.45	1.2	6(d)
$+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{O}_3+\text{Ti}(\text{iv})\text{O}_2$	0.70	0.56	0.50	1.2	6(e)
$+\text{Ti}(\text{bh})[\text{Ti}(\text{iv})]\text{Ti}(\text{ih})\text{O}_5$	0.93	0.58	0.52	1.2	6(f)
$+\text{Ti}(\text{bv})\text{Ti}(\text{iv})\text{O}_3+\text{Ti}(\text{iv})\text{O}_2$	1.09	0.63	0.58	1.3	6(g)
$+\text{Ti}(\text{iv})_2\text{O}_3+\text{Ti}(\text{bv})\text{O}_2$	1.04	0.81		1.5	6(h)
$-\text{Ti}(\text{bh})\text{O}_2-\text{O}$	0.26	0.85	0.96	1.7	6(i)
$+\text{Ti}(\text{iv})_2\text{O}_3\cdot\text{Ti}(\text{ih})\text{O}_2$	1.35	1.20		1.9	6(j)
Total cell z (Å)	22.96	29.52	36.08		

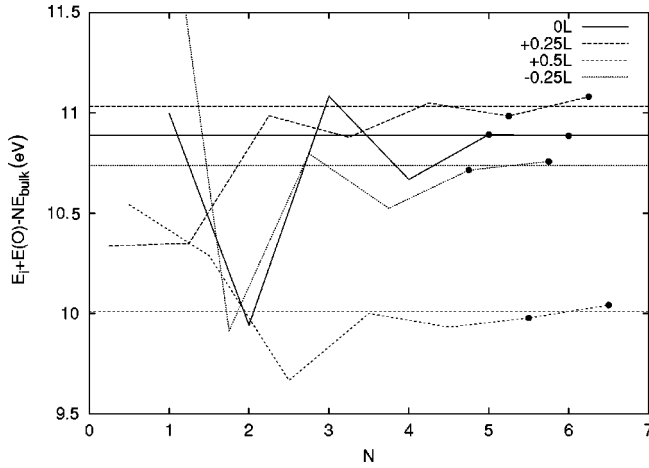


FIG. 7. Estimating surface energies by the method described in Sec. II C. Data are presented for four low-energy reduced reconstructions, one from each class: $\pm 0/\square_{\text{O}} - \text{O}_2\text{O} \rightarrow \text{O}'$; $+0.25/\square_{\text{O}} + \text{Ti}(\text{iv})\text{O}_2 - \text{O}$; $+0.5/\square_{\text{O}} + \text{Ti}(\text{iv})_2\text{O}_3$; $-0.25/\square_{\text{O}} [+ \text{Ti}(\text{iv})\text{O}_2]_2\text{Ti}(\text{iv})\text{O}$. For each reconstruction, absolute energies E_i are scaled according to Eq. (2) and plotted against slab thickness (N). E_{surf} is obtained by averaging the data from the thickest slabs (filled circles).

tion between the two reconstructions $-\text{Ti}(\text{bv})\text{O}_2 - \text{O}$ and $-\text{O}_{\text{sub}}$ [Figs. 6(d) and 3(c)]. These are practically isoenergetic ($\Delta E_{\text{surf}} = 1.1\text{--}1.2$ eV) and this suggests a propensity for vertical half ribbons to form in any rutile channel, at bulk or interstitial sites. Within rutile ribbons, Ti-O distances of 2.0 Å, Ti-Ti of 3.0 Å, and Ti-O-Ti angles of 100° are computed.

The other structural extreme is cubic TiO rocksalt. While this shows similar Ti-O (2.1 Å), the Ti-O-Ti angles are smaller (90°) and Ti-Ti are shorter (2.7–2.8 Å) than in rutile ribbons (both computed and experimental data). In our computed reconstructions, distortion to $(90 \pm 5)^\circ$ ribbon angles and short Ti-Ti are features of mixed bulk-interstitial reconstructions, as presented in Sec. III D and Fig. 9. It seems, therefore, that occupation of interstices can result in rocksalt segments.

Our approach, therefore, is to rationalize the structure and energetics of computed reconstructions as resulting from rutilelike or rocksaltlike elements. A similar interpretation has been applied to vanadium oxide surfaces: various cleavages of VO and VO_2 are calculated to be responsible for reconstructions on V_2O_3 .⁵⁵ The [001] rows of Ti(iv) and Ti(ih) may be considered to be dislocations, one-dimensional surface analogs of the shear planes of Magnéli phases. We will now examine some of the factors affecting the energy of formation of a dislocation and extend these ideas to the computed energetics of this study.

C. Energy of dislocation

In the bulk rutile structure, Ti(bh) and Ti(bv) octahedra share corners along $[1\bar{1}0]$ and $[110]$. By contrast, the interstitial octahedra share edges and faces with the surrounding bulk octahedra. Occupation of an interstice by Ti(ih) or Ti(iv) thus increases Ti-Ti connectivity: compared to the

corner-sharing case, Ti-Ti distance is shorter across a shared edge, and shorter again across a shared face. Considering delocalized electronic bands, enhanced Ti-Ti connectivity causes a widening of the conduction band and narrowing of the band gap.⁵⁴ As the bottom of the conduction band is partially occupied in these reduced systems, there is a correspondent lowering of the total energy. Balancing this from the purely ionic viewpoint, Ti-Ti repulsion will be high across edges, and even higher across shared faces. There are thus two competing influences on the energetics of dislocation.

In the reduced bulk, these competing factors dictate the equilibrium between random Ti interstitials and ordered shear planes. At the reduced (110) surface, dislocation is the favored mode of reconstruction and a wide variety of reconstructions featuring dislocations [i.e., Ti(iv), Ti(ih)] are of comparable stability ($\Delta E_{\text{surf}} = 0.7\text{--}1.3$ eV, Sec. III D, Fig. 8). In all of these cases ions are constrained and forced to form rocksalt segments: for instance, little Ti relaxation is possible within the horizontal ribbons of $+\text{Ti}(\text{ih})\text{O}$ and $+\text{Ti}(\text{bh})\text{Ti}(\text{ih})\text{O}_3$ [Figs. 4(d) and 5(b)]. A similar level of strain is caused within a (110) layer by removal of bridging O [Fig. 3(b), $\Delta E_{\text{surf}} = 0.9$ eV].

On the other hand, dislocation to the vertically oriented interstice opens up a new degree of freedom: $[110]$ relaxation. Thus in $+\text{Ti}(\text{iv})\text{O}_2$ the cation relaxes into the upper part of the interstice, giving relatively long Ti-Ti across the edges and faces shared with the layer below (Sec. III E). The result is that this dislocation decorates surfaces at an average cost of only 0.1 ± 0.1 eV.⁵³

We can, therefore, view $+\text{Ti}(\text{iv})_2\text{O}_3$ as a “twinned dislocation.” By twinning, $\square_{\text{O}}$ is eliminated, a symmetric (1×2) planar pattern is formed and both Ti(iv) face share with only one of the Ti(bh) of the layer below [Fig. 5(a)]. Vertical relaxation [Ti(iv) upwards, Ti(bh) downwards] relieves the strain observed otherwise in rocksalt segments. These factors combine to give the ca. 1 eV stabilization (Sec. III B) and make $+\text{Ti}(\text{iv})_2\text{O}_3$ the most stable $(1 \times 2)\square_{\text{O}}$ -reduced surface.

There are three other possible twinned dislocations on rutile (110). $+\text{Ti}(\text{ih})_2\text{O}_3$ [Fig. 5(f)] is quite stable: while the Ti(ih) also face shares with just one of the Ti(bv) of the sublayer, the 1.1 eV ΔE_{surf} is probably due to limited relaxation within horizontal ribbons. Neither of the symmetric twinned dislocations that face share with two sublayer Ti are stable. $+\text{Ti}(\text{iv})_2\text{O}_3$ about Ti(bv) distorts to $+\text{Ti}(\text{iv})\text{O}_2\text{Ti}(\text{iv})\text{O}_2$ (stoichiometric⁴⁶), while $+\text{Ti}(\text{ih})_2\text{O}_3$ about Ti(bh) [Fig. 5(n)] rearranges completely to give $+\text{Ti}(\text{iv})_2\text{O}_3$ about Ti(bh).

D. Electron distribution

While the bonding in stoichiometric TiO_2 is in fact mixed ionic covalent,²⁸ to a first approximation the conduction band is of predominantly Ti:*d* character and the cations may be represented as Ti^{4+} . For many applications—such as parametrizing Ti-O potentials—an important question is how this picture changes at a reduced rutile surface. A thorough analysis of the electronic structure of such surfaces is the subject

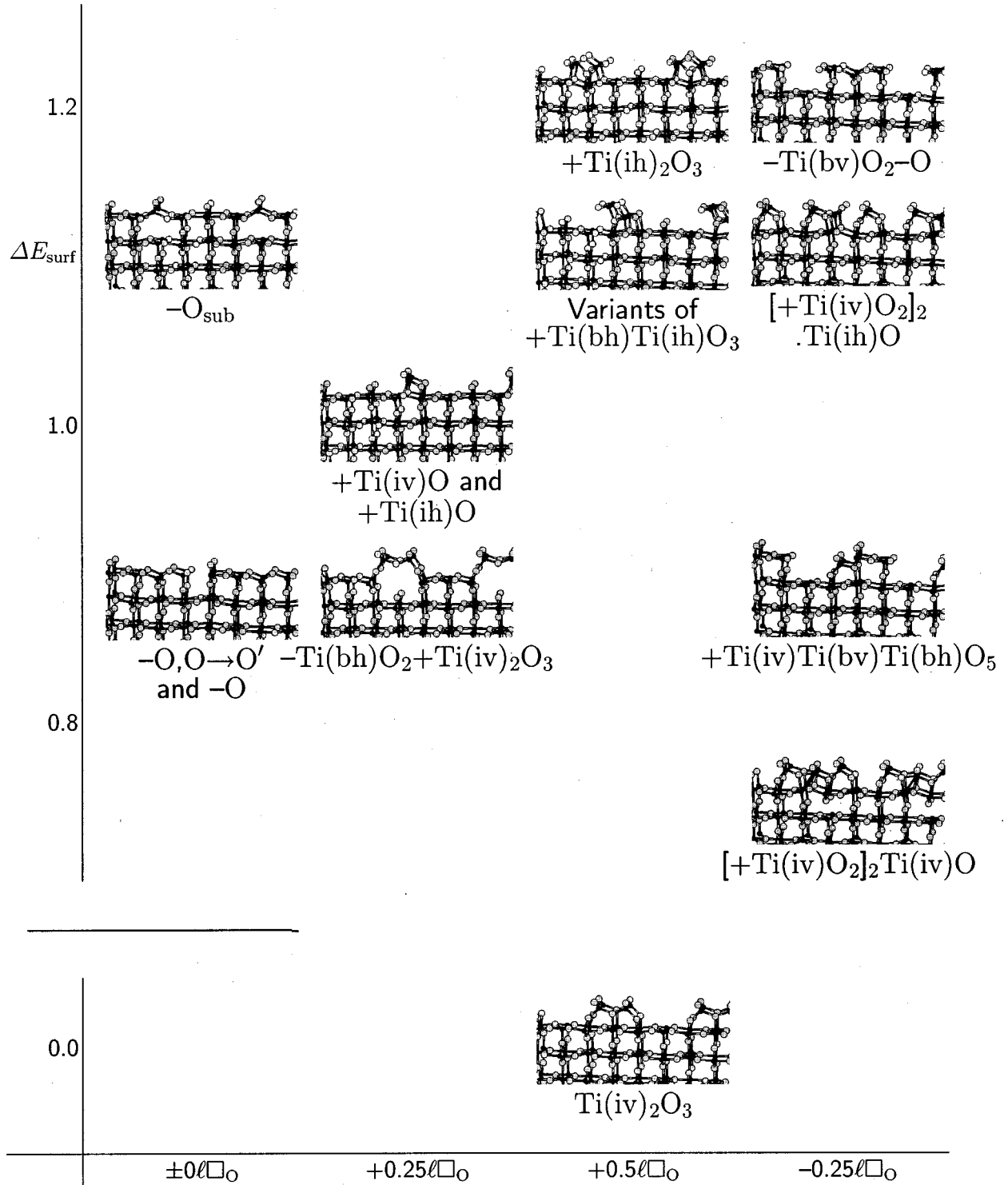


FIG. 8. Schematic energetics [eV per (1×2) surface section] of some of the most stable stoichiometric reconstructions found in this work. Some reconstructions have been omitted for want of space, in particular, those formed by the addition of $Ti(iv)O_2$. Note the break in the ΔE_{surf} axis. For exact energies and full list of isomers, see Tables II–V and Figs. 3–6.

of future work, but we will identify some trends from the structures and energetics presented here.

We consider reconstructed and $\Box_{\text{O}}$ -reduced surfaces with two electrons per (1×2) cell occupying states at the lower edge of the conduction band. Clearly, these states are localized to some degree near the reconstructed surface. It is,

therefore, tempting to assign formal charges to the cations of the reconstruction, giving $(Ti^{3+}:[Ar]4s^23d^1)_2$ or $Ti^{2+}:[Ar]4s^23d^2$, the underlying assumption being a reconstructed overlayer of different oxidation state and different chemistry.⁵⁶ Is there any evidence for such an assignment?

As noted in Sec. III B, there are no significant differences

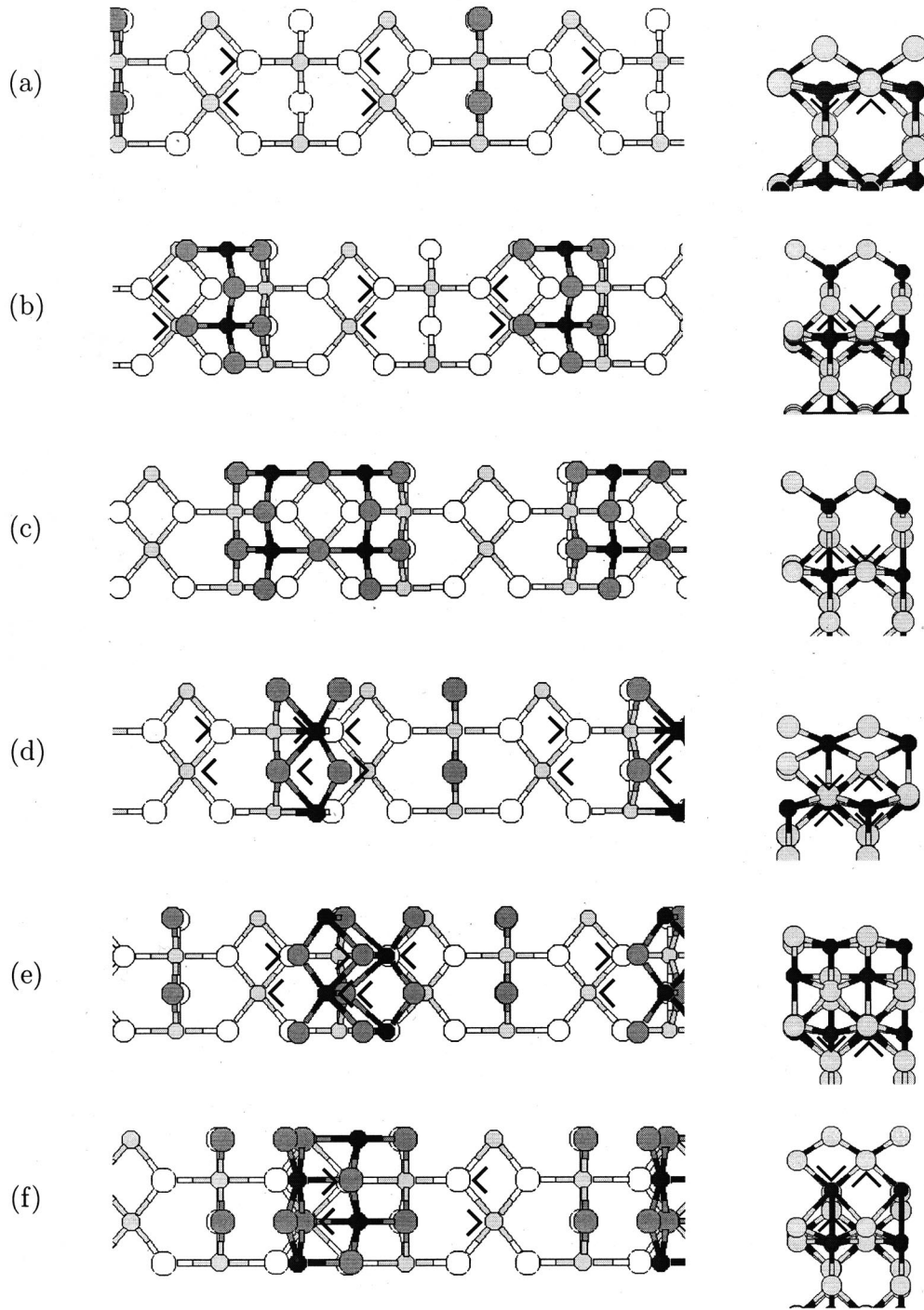


FIG. 9. Views of low-energy reduced surfaces (the reconstruction and one sublayer) showing ribbons distorted to right angles ($90 \pm 5^\circ$). Undistorted rutile ribbons show angles of 100° (bulk, slab horizontal) and 110° (even-layered slab, vertical). In the top view along $z = [110]$, the sublayer is shaded lightly. The side view is along $y = [1\bar{1}0]$. (a) —O , Fig. 3(b); (b) $+\text{Ti(IV)}\text{O}_2\text{—O}$, Fig. 4(c); (c) $+\text{Ti(IV)}_2\text{O}_3$, Fig. 5(a); (d) $+\text{Ti(IV)}\text{O}$, Fig. 4(d); (e) $+\text{Ti(bh)Ti(IV)}\text{O}_3$, Fig. 5(b); (f) $+\text{Ti(bv)Ti(IV)}\text{O}_3$, Fig. 5(g).

between the optimized geometry of the reduced $+\text{Ti(IV)}_2\text{O}_3$ reconstruction and those of similar stoichiometric structures $+\text{Ti(IV)}\text{O}_2$ and $+\text{Ti(IV)}_2\text{O}_3 + \text{O}$.²⁶ In a great many isomers the same decorations are found on the reduced and stoichiometric surfaces (Sec. III E). This is contrary to the major difference that would be expected from a simple ionic viewpoint upon reduction to Ti^{3+} or Ti^{2+} . It also in-

dicates that the spin state plays a negligible role (see also Table I).

In a localized picture, $+0.25/\square_{\text{O}}$ reconstructions are $[\text{Ti}^{2+}\text{O}^{2-}]$ and $+0.5/\square_{\text{O}}$ are $[\text{Ti}_2^{3+}\text{O}_3^{2-}]$. However, we find that $+0.25/\square_{\text{O}}$ reconstructions are not abruptly different from $+0.5/\square_{\text{O}}$ and so it is unlikely that the oxidation states differ in this way. Generally, we observe consistent patterns

of bonding across the four classes of reduced reconstruction, which suggests that their electronic structure is broadly the same. This is only possible if there is delocalization across ions of the reconstruction and of the complete layer below. It is these layers, therefore, that comprise the oxide “surface” and the major contribution to E_{surf} is due to the structure of these surface layers.

We note in Sec. IV C that many reduced reconstructions may be classified as dislocations or rocksalt segments. The situation must, therefore, be similar to that in the Magnéli phases of the reduced bulk, with excess electron density on Ti layers on *both* sides of the shear plane of anions and associated with the strained geometries of edge- and face-sharing octahedra.

Cursory analysis of the occupied conduction-band states that we have computed confirms their delocalized nature. Other first-principles studies on reduced rutile concur that the occupied states at the bottom edge of the conduction band are delocalized over the surface and subsurface layers and that the role of spin is negligible.^{57,58} However, density-functional theory is known to overdelocalize electrons, so that ultimately this question can not be resolved at this level of approximation.

V. CONCLUSIONS

We present, to our knowledge, the first compendium of stable (1×2) reconstructions on the reduced (110) surface of TiO_2 rutile. The data come from a comprehensive computational survey of about 100 possible (1×2) surface reconstructions, sorted according to first-principles surface energy and rationalized in terms of common structural features.

The central result of this work is that the most stable $\square_{\text{O}}$ -reduced (1×2) reconstruction is the double row of added suboxide proposed by Onishi and Iwasawa,¹² which we denote by $+\text{Ti}(\text{iv})_2\text{O}_3$. The surface energy is estimated to be $3.29 \pm 0.08 \text{ J m}^{-2}$. Surface reduction and reconstruction is calculated to cost about 5.4 eV per $1/2(\text{O}_2)$ desorbed.

We find a wide variety of other (1×2) reduced reconstructions and the discussion in this paper is limited to the most stable of these, namely the 56 isomers in the surface energy range 3.6–4.1 J m^{-2} . Analysis of isomers so closely spaced in energy is only possible if surface energies are estimated accurately, which justifies the careful approach developed in our earlier work.²⁶ We recognize, however, that our economical treatment of reciprocal space means that some uncertainty remains in the exact energy values quoted. The closeness in energy implies that many of these structures are candidates for the immediate kinetic products of O desorption and for the reactive (1×2) phases observed in experiment. However, on annealing in vacuum, all (1×2) iso-

mers should reconstruct to the thermodynamically favored $+\text{Ti}(\text{iv})_2\text{O}_3$.

While bulk-terminated structures with a simple O vacancy are among these isomers, the partially reduced surface shows a great deal more structural richness, perhaps the product of interplay between the extreme cases of stoichiometric rutile and reduced rocksalt. We find that most of the computed reconstructions can be described as combinations of structural elements such as dislocations, bulklike units, and $\text{Ti}(\text{iv})\text{O}_2$ decorations. Dislocations (i.e., $[001]$ rows of interstitial Ti) are computed to occur at the surface at little energetic cost, probably because of compensating bonding/repulsion effects as Ti-Ti connectivity is enhanced. Twinned dislocations can further reduce Ti-Ti repulsion. Should dislocations form as “vertical” Ti-O ribbons perpendicular to the surface, we suggest that relaxation of Ti away from the surface can be another source of stabilization. Together these factors account for the unusual stability of $+\text{Ti}(\text{iv})_2\text{O}_3$. By contrast, distortion or disruption of the O sublattice is energetically unfavored. Indeed, extreme cation polarizability within a rigid anion sublattice is a well-known property of TiO_2 ,⁵⁹ ultimately responsible for its use as a white pigment.

In agreement with our previous findings for stoichiometric systems, we note that the most stable reduced rutile surface is not the one with the maximum number of anions coordinated directly to each surface Ti. For instance, within rutile ribbons and $\text{Ti}(\text{iv})\text{O}_2$ tetrahedra fourfold coordination is common. The fivefold-coordinated $\text{Ti}(\text{bh})$ cation occurs in the most stable (110) surfaces of both stoichiometric (1×1) and $\square_{\text{O}}$ -reduced (1×2) . This is further evidence that bonding in titanium oxides is mixed ionic-covalent. Of course, this finding may be in error if first-principles methods overestimate covalent Ti-O overlap.

We can speculate that, under high-temperature annealing, random Ti interstitial defects diffuse from the bulk and segregate at the surface, self-organizing into $[001]$ dislocations, (1×2) twinned rows, and the other ordered patterns observed in experiment. These are the surface analogs of the ordered shear planes in the bulk that characterize Magnéli phases. This study thus raises new questions about the dynamics of bulk-surface equilibria and surface redox reactions.

ACKNOWLEDGMENTS

This project was funded by Enterprise Ireland (SDE). We have benefitted from generous allocations of computer time at the Department of Chemistry (TCD), the Trinity Center for High Performance Computing and the Edinburgh Parallel Computing Center. We acknowledge the support of the European Commission through Grant No. HPRI-1999-CT-00026 (the TRACS program at EPCC).

*Present address: NMRC, University College Cork - National University of Ireland, Cork, Lee Maltings, Prospect Row, Cork, Ireland. FAX: +353-21-4270271. Electronic address: Simon.Elliott@nmrc.ucc.ie

[†]FAX: +44-131-6505902; Electronic address: S.P.Bates@ed.ac.uk

¹K. Fukui, H. Onishi, and Y. Iwasawa, Phys. Rev. Lett. **79**, 4202 (1997).

²M. Ashino, T. Uchihashi, K. Yokoyama, Y. Sugawara, S. Morita,

- and M. Ishikawa, Phys. Rev. B **61**, 13 955 (2000).
- ³M. Li, W. Hebenstreit, and U. Diebold, Phys. Rev. B **61**, 4926 (2000).
- ⁴C. L. Pang, S. A. Hancock, H. Raza, G. Thornton, O. Gülseren, R. James, and D. W. Bullett, Surf. Sci. **437**, 261 (1999).
- ⁵R. E. Tanner, M. R. Castell, and G. A. D. Briggs, Surf. Sci. **437**, 263 (1999).
- ⁶C. L. Pang, S. A. Haycock, H. Raza, P. W. Murray, G. Thornton, O. Gulseren, R. James, and D. W. Bullett, Phys. Rev. B **58**, 1586 (1998).
- ⁷M. Li, W. Hebenstreit, U. Diebold, M. A. Henderson, and D. R. Jennison, Faraday Discuss. **114**, 245 (1999).
- ⁸M. Li, W. Hebenstreit, L. Gross, U. Diebold, M. A. Henderson, D. R. Jennison, P. A. Schultz, and M. P. Sears, Surf. Sci. **437**, 173 (1999).
- ⁹R. E. Tanner, M. R. Castell, and G. A. D. Briggs, Surf. Sci. **412/413**, 672 (1998).
- ¹⁰P. W. Murray, N. G. Condon, and G. Thornton, Phys. Rev. B **51**, 10 989 (1995).
- ¹¹R. A. Bennett, P. Stone, N. J. Price, and M. Bowker, Phys. Rev. Lett. **82**, 3831 (1999).
- ¹²H. Onishi and Y. Iwasawa, Surf. Sci. **313**, L783 (1994).
- ¹³C. Xu, X. Lai, G. W. Zajac, and D. W. Goodman, Phys. Rev. B **56**, 13 464 (1997).
- ¹⁴H. Onishi and Y. Iwasawa, Surf. Sci. **357-358**, 773 (1996).
- ¹⁵Q. Guo, I. Cocks, and E. M. Williams, Phys. Rev. Lett. **77**, 3851 (1996).
- ¹⁶R. A. Bennett, P. Stone, and M. Bowker, Faraday Discuss. **114**, 267 (1999).
- ¹⁷P. Stone, R. A. Bennett, and M. Bowker, New J. Phys. **1**, 1.1 (1999).
- ¹⁸P. J. Möller and M. C. Wu, Surf. Sci. **224**, 265 (1989).
- ¹⁹A. Szabo and T. Engel, Surf. Sci. **329**, 241 (1995).
- ²⁰M. A. Henderson, Surf. Sci. **419**, 174 (1999).
- ²¹M. Li, W. Hebenstreit, U. Diebold, A. M. Tyryshkin, M. K. Bowman, G. G. Dunham, and M. A. Henderson, J. Phys. Chem. B **104**, 4944 (2000).
- ²²S. Fischer, A. W. Munz, K.-D. Schierbaum, and W. Göpel, Surf. Sci. **337**, 17 (1995).
- ²³E. Landree, L. D. Marks, P. Zshack, and C. J. Gilmore, Surf. Sci. **408**, 300 (1998).
- ²⁴D. Novak, E. Garfunkel, and T. Gustafsson, Phys. Rev. B **50**, 5000 (1994).
- ²⁵A. Howard, C. E. J. Mitchell, D. Morris, R. G. Egdel, and S. C. Parker, Surf. Sci. **448**, 131 (2000).
- ²⁶S. D. Elliott and S. P. Bates, Surf. Sci. **495**, 211 (2001).
- ²⁷K.-O. Ng and D. Vanderbilt, Phys. Rev. B **56**, 10 544 (1997).
- ²⁸C. N. R. Rao and B. Raveau, *Transition Metal Oxides: Structure, Properties, and Synthesis of Ceramic Oxides* (Wiley-VCH, New York, 1998).
- ²⁹M. A. San Miguel, C. J. Calzado, and J. F. Sanz, J. Phys. Chem. B **105**, 1794 (2001).
- ³⁰V. E. Henrich and R. L. Kurtz, Phys. Rev. B **23**, 6280 (1981).
- ³¹P. J. D. Lindan, N. M. Harrison, M. J. Gillan, and J. A. White, Phys. Rev. B **55**, 15 919 (1997).
- ³²M. Ramamoorthy, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. B **49**, 7709 (1994).
- ³³J. Purton, D. W. Bullett, P. M. Oliver, and S. C. Parker, Surf. Sci. **336**, 166 (1995).
- ³⁴U. Diebold, J. F. Anderson, K.-O. Ng, and D. Vanderbilt, Phys. Rev. Lett. **77**, 1322 (1996).
- ³⁵O. Gülseren, R. James, and D. W. Bullett, Surf. Sci. **377-379**, 150 (1997).
- ³⁶A. T. Paxton and L. Thiên-Nga, Phys. Rev. B **57**, 1579 (1998).
- ³⁷D. Jung, H.-J. Koo, D. Dai, and M.-H. Whangbo, Surf. Sci. **473**, 193 (2001).
- ³⁸M. J. Gillan, J. Phys.: Condens. Matter **1**, 689 (1989).
- ³⁹G. Kresse and J. Hafner, Phys. Rev. B **49**, 14 251 (1994).
- ⁴⁰G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
- ⁴¹G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
- ⁴²J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- ⁴³G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
- ⁴⁴H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- ⁴⁵K. M. Glassford, N. Troullier, J. L. Martins, and J. R. Chelikowsky, Solid State Commun. **76**, 635 (1990).
- ⁴⁶See EPAPS Document No. E-PRBMDO-65-016224 for (I) less stable reduced reconstructions ($\Delta E_{\text{surf}} > 2.0$ eV) and (II) additional stoichiometric reconstructions not included in Ref. 26. This document may be retrieved via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory /epaps/. See the EPAPS homepage for more information.
- ⁴⁷J. C. Boettger, Phys. Rev. B **49**, 16 798 (1994).
- ⁴⁸J. C. Boettger, J. R. Smith, U. Birkenheuer, N. Rösch, S. B. Trickey, J. R. Sabin, and S. P. Apell, J. Phys.: Condens. Matter **10**, 893 (1996).
- ⁴⁹V. Fiorentini and M. Methfessel, J. Phys.: Condens. Matter **8**, 6525 (1996).
- ⁵⁰V. Fiorentini and M. Methfessel, J. Phys.: Condens. Matter **10**, 895 (1996).
- ⁵¹G. Herzberg, *Molecular Spectra and Molecular Structure: 1. Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).
- ⁵²E. P. F. Lee, P. Soldán, and T. G. Wright, Chem. Phys. Lett. **295**, 354 (1998).
- ⁵³S. D. Elliott and S. P. Bates, Phys. Chem. Chem. Phys. **3**, 1954 (2001).
- ⁵⁴P. A. Cox, *The Electronic Structure and Chemistry of Solids* (Oxford University Press, Oxford, 1987).
- ⁵⁵G. Kresse, S. Surnev, M. G. Ramsey, and F. P. Netzer, Surf. Sci. **492**, 329 (2001).
- ⁵⁶C. B. Duke, Chem. Rev. **96**, 1237 (1996).
- ⁵⁷P. J. D. Lindan and N. M. Harrison, Surf. Sci. **479**, L375 (2001).
- ⁵⁸T. Albaret, F. Finocchi, C. Noguera, and A. De Vita, Phys. Rev. B **65**, 035402 (2002).
- ⁵⁹*Nonstoichiometric Oxides*, edited by O. T. Sørensen (Academic, New York, 1981).
- ⁶⁰In terms of the nomenclature specific to unreconstructed surfaces, “six-coordinate Ti” with “bridging O” belongs to a vertical octahedron, while the “five-coordinate Ti” between “in-plane O” is in a horizontal octahedron.
- ⁶¹ $E(\text{O}:^3P) = -1.971 \pm 0.003$ eV from isolated atom (six-electron pseudopotential) in cubic supercell of sides 20–30 Å.