

# A density functional study of clean and hydrogen-covered $\alpha$ -MoO<sub>3</sub>(010): Electronic structure and surface relaxation

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We report extensive density functional theory calculations, using pseudopotentials with a plane-wave basis, for the properties of the (010) face of molybdenum trioxide ( $\alpha$ -MoO<sub>3</sub>). The surface is modeled by a one-layer slab. Calculated bond lengths compare favorably with experimental measurements. The bonding of the different oxygen species to molybdenum is analyzed using the crystal orbital overlap population. This analysis indicates that the bonding is a combination of ionic and covalent character for all oxygen species. The terminal oxygen exhibits covalent bonding to Mo which is stronger than either of the two bridging oxygens. We also study the adsorption of hydrogen on this surface. Hydrogen is most strongly adsorbed over the terminal oxygen, followed by the asymmetric bridging oxygen, and then the symmetric bridging oxygen. This trend is explained in terms of simple chemical concepts. The inclusion of full surface relaxation is important for even a qualitative description of adsorbate bonding. © 1998 American Institute of Physics. [S0021-9606(98)01640-7]

## I. INTRODUCTION

One of the most important problems in heterogeneous catalysis is the partial oxidation of small hydrocarbons such as methane. Molybdenum trioxide ( $\alpha$ -MoO<sub>3</sub>) has been shown to be active in partially oxidizing methane to formaldehyde,<sup>1-4</sup> but the mechanism by which this transformation takes place is not fully understood and there is considerable controversy regarding the nature of the active oxygen.  $\alpha$ -MoO<sub>3</sub>, along with MoO<sub>2</sub>, are the two molybdenum oxides stable above 1000 °C, and it is likely that  $\alpha$ -MoO<sub>3</sub> is an active species in many catalytic reactions involving molybdenum oxides. There are several types of oxygen sites in  $\alpha$ -MoO<sub>3</sub> available for reaction, but it is not clear which sites participate in the reaction.

Bulk  $\alpha$ -MoO<sub>3</sub> is a layered material, with bilayers parallel to the (010) plane (Fig. 1). The bilayers, coupled together by weak van der Waals forces, consist of repeating units of MoO<sub>6</sub> quasi-tetrahedra, with several oxygen atoms shared between the two Mo atoms. In particular, there are three distinct types of oxygen atoms.<sup>5</sup> First, there is a terminal oxygen bonded to only one Mo atom with a distance of 1.67 Å. Second, there are symmetrically bridging oxygens bonded equidistant to two Mo atoms (1.95 Å) and weakly bonded to a third Mo atom (2.33 Å). Finally, there are asymmetric bridging oxygen atoms bonded to two Mo atoms with bond

lengths of 1.74 and 2.25 Å. In order to elucidate the activity of  $\alpha$ -MoO<sub>3</sub> for partial oxidation one must understand the chemical nature of each of the distinct oxygen species. For example, it has been proposed that the terminal oxygen is the active species in partial oxidation.<sup>6</sup> Therefore the (010) surface, which has terminal oxygens exposed, should be the most reactive face for partial oxidation.

There has been a number of experimental studies on  $\alpha$ -MoO<sub>3</sub>; most are studies of supported MoO<sub>3</sub> where the detailed surface structure is unknown. Experimentally, molybdenum oxides with varying concentrations of terminal oxygens are synthesized and differences in product distributions and activity are measured.<sup>6,7</sup> However, such studies do not provide information as to the specific roles of the various surface sites or the changes in the catalyst along the course of reaction.

In this paper we study the  $\alpha$ -MoO<sub>3</sub>(010) surface using density functional theory calculations, taking into account full relaxation of the surface. An analysis of the covalent bonding of each Mo–O bond reveals that bond length is not an accurate gauge of the amount of covalent bonding present. To examine the chemical reactivity of each type of oxygen the adsorption of hydrogen over different oxygen sites is studied. Full relaxation of the MoO<sub>3</sub> surface upon bonding to hydrogen is found to be important: The relaxation of the ions qualitatively changes the relative O–H bond energies for the different types of oxygen compared to the unrelaxed slab.

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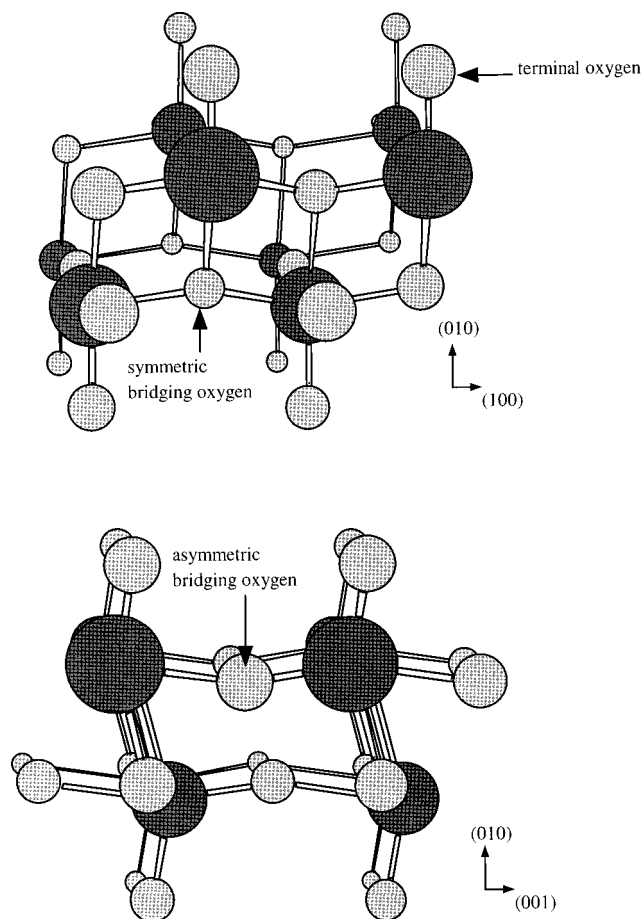


FIG. 1. The one-layer model of the clean (010)  $\alpha$ -MoO<sub>3</sub> surface used in the calculation. The three distinct types of oxygen are noted. The dark grey balls are Mo atoms, the white balls are hydrogen atoms, and the light grey balls are oxygen atoms.

## II. COMPUTATIONAL DETAILS

All calculations were performed using the commercially available version of CASTEP,<sup>8,9</sup> a density functional plane-wave pseudopotential code. In these calculations, the local-density approximation is used for electron exchange and correlation. The bare MoO<sub>3</sub> slab and the MoO<sub>3</sub>+H systems were relaxed until the forces on all atoms were less than 0.05 eV/atom. The optimized norm-conserving pseudopotential for Mo including states up to 4*d* was generated with  $r_{c,s} = r_{c,p} = r_{c,d} = 1.7$  a.u. from a singly ionized reference configuration of [Kr]4*s*<sup>2</sup>4*p*<sup>6</sup>4*d*<sup>5</sup> and is expressed in the fully separable Kleinman–Bylander form.<sup>10</sup> Optimization<sup>11</sup> was performed with  $q_{c,s} = q_{c,d} = 6.5$  Ry<sup>1/2</sup> and  $q_{c,p} = 7.5$  Ry<sup>1/2</sup> and 6, 4, and 4 Bessel functions for the *s*, *p*, and *d* orbitals, respectively. The soft oxygen pseudopotential was generated according to the scheme of Troullier and Martins<sup>12</sup> with core radii  $r_{c,s} = 1.3$  and  $r_{c,p} = 1.65$  a.u. For hydrogen, a filtered Coulomb potential was used.

The model for the  $\alpha$ -MoO<sub>3</sub> surface consists of a single layer of the (010) face, repeated periodically in three dimensions with about 14 Å of vacuum between layers. Four special *k* points in the irreducible Brillouin zone were used with a 700 eV cutoff for the plane-wave basis states. For the adsorption of hydrogen, a coverage was used where one hydro-

TABLE I.  $\alpha$ -MoO<sub>3</sub> (010) bond lengths (in Å).

Type of oxygen	Calculated		Experiment (Ref. 5)	% error
	Slab	Bulk		
Symmetric bridging	1.92	1.94	1.95	-0.5
	2.30	2.32	2.33	-0.4
Asymmetric bridging	1.76	1.75	1.73	+1.1
	2.19	2.24	2.25	-0.4
Terminal	1.67	1.67	1.67	0.0

gen atom was adsorbed per type of oxygen atom, on one side of the slab. As a test of these pseudopotentials, the equilibrium lattice parameters of the  $\alpha$ -MoO<sub>3</sub> bulk system was determined by keeping the ratio of the lattice vectors fixed to the experimental value, and finding the volume which minimizes the total energy. The equilibrium volume was found to be 191.0 Å<sup>3</sup>, slightly lower than the experimental value of 203.0 Å<sup>3</sup>.<sup>5</sup> We fix the lattice parameters at the experimental values for subsequent calculations of the MoO<sub>3</sub> surface. Relaxation of the ionic positions at the experimental lattice constant yields bond lengths in excellent agreement with experimental values (Table I).

For the analysis of covalent bonding, the crystal orbital overlap population (COOP) was calculated. The COOP, originally developed by Hoffman,<sup>13</sup> is a projection of two atomic orbitals onto the final wave function, weighted by the overlap of the two orbitals. This projection gives an indication of the bonding or antibonding nature of the interaction of the two orbitals. A positive value of the COOP indicates a bonding interaction, and a negative value means that there is an antibonding interaction. The magnitude of the COOP curves is also an indication of the relative amount of covalent bonding. To calculate the COOP from a plane-wave calculation, atomic orbitals are constructed from the pseudo-wave functions. These orbitals are made to satisfy Bloch's theorem by summing over nearest cells with the application of a *k*-point dependent phase factor. The COOP is then calculated by the following equation:

$$\text{COOP}_{ij}(\epsilon) = \sum_{kn} \langle \psi_{kn} | \phi_{ik}^a \rangle \langle \phi_{jk}^b | \psi_{kn} \rangle S_{ij} \delta(\epsilon - \epsilon_{kn}),$$

where  $\phi_{ik}^a$  is the atomic orbital centered on atom *a*, *n* is the band index, and  $S_{ij}$  is the overlap matrix between atomic orbitals. This method of calculating the COOP is designed to yield only a qualitative picture of the bonding. The value of the COOP can be understood in the following manner. We can write the crystal orbitals as a linear combination of atomic orbitals:

$$\psi_{kn} = \sum_i c_{ik} \phi_{ik}.$$

If the wave functions are normalized, the probability density of the crystal orbital is

$$\langle \psi_{kn} | \psi_{kn} \rangle = \sum_i |c_{ik}|^2 + \sum_{ij} c_{ik}^* c_{jk} S_{ij}.$$

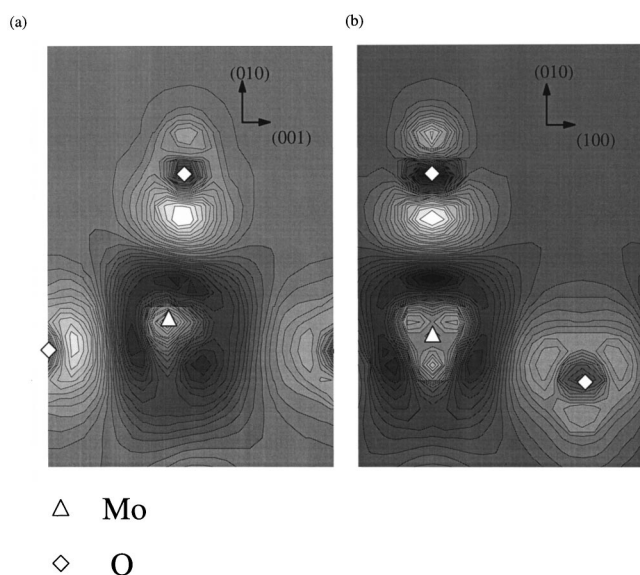


FIG. 2. Charge-density difference maps of the  $\alpha$ - $\text{MoO}_3$  (010) system, showing cuts through the different oxygen species. The triangles refer to the position of the Mo atoms, and the diamonds represent the position of the O atoms. Darker deviations from the background indicate a depletion of charge density, while lighter deviations indicate additional charge density. (a) Charge-density difference map of the terminal and symmetric bridging oxygens. (b) Charge-density difference map of the terminal and asymmetric bridging oxygens.

The first summation on the right-hand side is the net population centered on each atom, and the second term is the crystal orbital overlap population. Each term in the summation is an indication of the relative density between the atoms with respect to two atomic orbitals. If the COOP is negative, then there is density subtracted between the atoms, indicating a crystal orbital antibonding in character, whereas a positive COOP is characteristic of a bonding contribution to the crystal orbital from the two atomic orbitals.

### III. RESULTS

#### A. $\alpha$ - $\text{MoO}_3$ (010) slab

The validity of the one-layer model to represent the (010) surface is substantiated by the fact that the equilibrium bond lengths of relaxed  $\alpha$ - $\text{MoO}_3$  bulk and the single layer were almost identical, with an average deviation of less than 2% compared to x-ray crystallographic data (see Table I). This indicates that the bonding between layers is not strong and should not play a role in bonding between an adsorbate and the (010) surface. Therefore we take one layer as our model for the  $\text{MoO}_3$  surface.

Charge-density difference plots indicate that bonding between oxygen and Mo is partially ionic, since most of the electron density is added around the oxygen atoms and taken away around the Mo atoms (Fig. 2). These plots are the result of the difference in electron density of the individual atomic densities and the final electronic density. Darker areas indicate a depletion of electron density, while lighter areas indicate increases in electron density. It is clear that for all oxygens, electron density is transferred from the Mo centers to the oxygen centers, indicating ionic bonding. Also, a por-

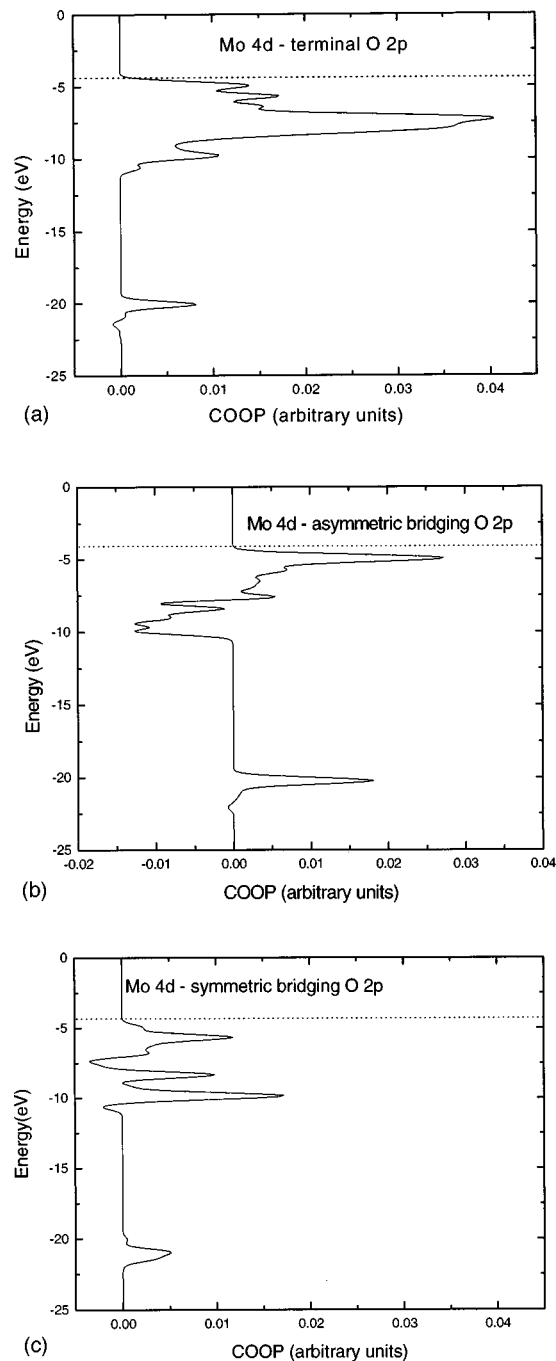


FIG. 3. (a) COOP between the Mo  $d$  orbitals and the terminal O  $2p$  orbitals. (b) COOP between the Mo  $d$  orbitals and the asymmetric O  $2p$  orbitals. (c) COOP between the Mo  $d$  orbitals and the symmetric O  $2p$  orbitals. The dotted line indicates the position of the Fermi level.

tion of the electron density is also found between the oxygens, although it is difficult to judge the relative magnitudes of the covalent contribution from the density difference plots alone. The COOP curves (Figs. 3 and 4) allow a more quantitative comparison of the relative amounts of covalent bonding present. The main differences in bonding between the Mo atom and the various oxygens lie in the Mo  $4d$ -O  $2p$  as well as the Mo  $5p$ -O  $2p$  interaction. The COOP of the Mo  $4d$ -O  $2p$  for the asymmetric and symmetric bridging oxygens reveal a weak, approximately equal covalent bonding between the bridging oxygens and the Mo  $4d$  orbital. On the

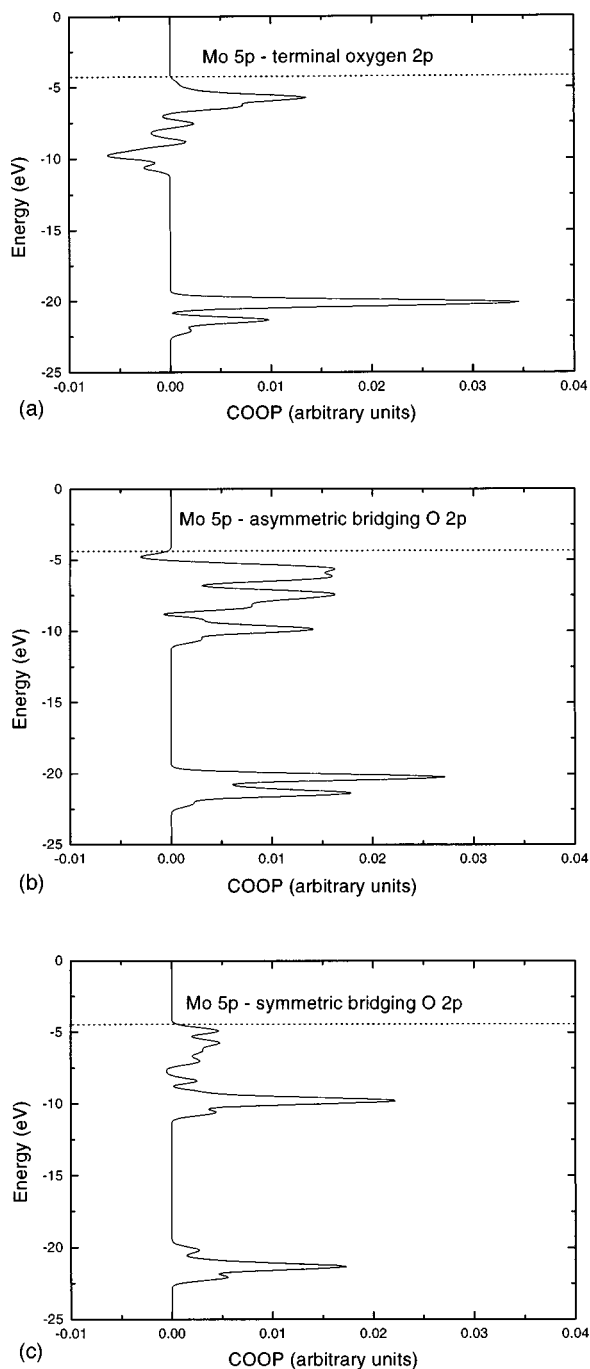


FIG. 4. (a) COOP between the Mo  $p$  orbitals and the terminal O  $2p$  orbitals. (b) COOP between the Mo  $p$  orbitals and the asymmetric O  $2p$  orbitals. (c) COOP between the Mo  $p$  orbitals and the symmetric O  $2p$  orbitals. The dotted line indicates the position of the Fermi level.

other hand, the COOP of the Mo  $4d$ -O  $2p$  for the terminal oxygen shows a covalent bond strength much greater than for either bridging oxygen species (Table III). In contrast, the COOP of the Mo  $5p$ -O  $2p$  is interesting in that the strongest interaction between the two orbitals occurs in the asymmetric bridging oxygen. The terminal oxygen has little bonding present between the Mo  $5p$  and O  $2p$  orbitals. Taken as a whole, however, the strongest covalent bonding occurs in the terminal oxygen, followed by the asymmetric oxygen.

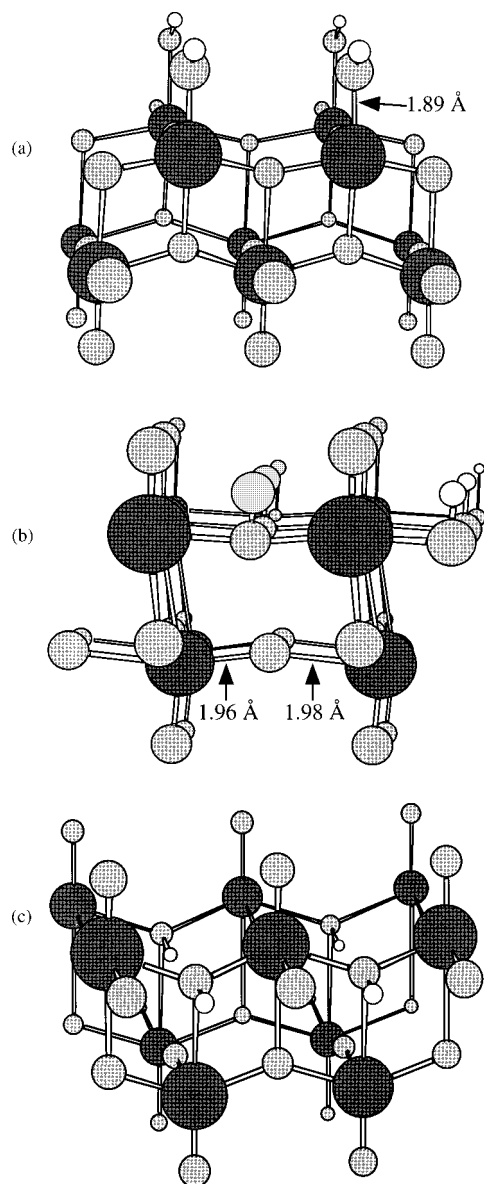


FIG. 5.  $\alpha$ -MoO<sub>3</sub>(010) with hydrogen. (a) Hydrogen adsorbed over terminal oxygen. (b) Hydrogen adsorbed over asymmetric bridging oxygen. (c) Hydrogen adsorbed over symmetric bridging oxygen.

The triply coordinated symmetric bridging oxygen has the smallest amount of covalent bonding.

## B. Adsorption of hydrogen on $\alpha$ -MoO<sub>3</sub>(010)

The most stable binding site for hydrogen on the MoO<sub>3</sub> slab is over the terminal oxygen, with a binding energy of  $-3.39$  eV. This strong binding is accompanied by lengthening of the Mo-O bond, from  $1.66$  to  $1.89$  Å (Fig. 5), while the hydrogen is bound to the oxygen at a distance of  $0.98$  Å. The asymmetric bridging oxygen binds hydrogen with an energy of  $-3.13$  eV. The Mo-O bond lengths for the asymmetric bridging oxygens become more symmetric, so that the oxygen is bound to two Mo atoms with bond lengths of  $1.96$  and  $1.98$  Å. Finally, hydrogen adsorption over the symmetric bridging oxygen is the most weakly bound species, with a binding energy of  $-2.77$  eV. Associated with this adsorption is a slight relaxation of the surface. A MoO<sub>3</sub> slab can be

TABLE II.  $\alpha$ -MoO<sub>3</sub> (010) with adsorbed hydrogen: Binding energies. All energies in eV.

Binding site	BE w/ full relax.	BE relax only H
Symmetric bridging O	-2.77	-2.22
Asymmetric bridging O	-3.13	-2.01
Terminal O	-3.39	-2.33

thought of as two sheets of Mo–O units linked together by the long Mo–O bond of the symmetric bridging oxygen. When hydrogen is adsorbed on the symmetrically bridging oxygen, the hydrogen is not bound perpendicular to the surface. Rather, the hydrogen is bound in the plane of the surface, perpendicular to the two symmetric bridging oxygen bonds. As a result of this bonding to hydrogen, the long bond of the symmetric bridging oxygen increases from 2.33 to 2.53 Å, effectively pulling the two sheets apart.

Calculations in which only the distance between the hydrogen and the surface was optimized illustrate the importance of surface relaxation for the adsorption of hydrogen on MoO<sub>3</sub>(010) (Table II). Without the inclusion of surface relaxation the calculated results are qualitatively different. First, the binding energies of the frozen surface +H calculations are much closer in energy than those with surface relaxation. This shows that there is a significant contribution from the rearrangement of surface atoms as a result of the presence of the adsorbate. Second, the ordering of the energies is different; allowing only H to relax, we find that the symmetric bridging oxygen site is more stable than the asymmetric bridging site, by 0.2 eV. With full surface relaxation, hydrogen over the asymmetric bridging oxygen is calculated to be more than 1 eV more stable than the symmetric bridging oxygen site. Furthermore, the differences in binding energy among the three types of oxygen sites are smaller, ranging from 0.12–0.32 eV, as compared to 0.26–0.62 eV for the fully relaxed system.

The bonding of the hydrogen to the three oxygen species is an interaction between the *s* orbital of hydrogen and the *p* orbitals of oxygen. Hydrogen above the asymmetric bridging oxygen is adsorbed directly above the oxygen, and thus is expected to interact with only one *p* orbital. This is borne out by the COOP plots (Fig. 6), where the only significant interaction occurs between the H *s* orbital and the O *p<sub>z</sub>* orbitals (*z* is taken to be perpendicular to the surface). The interaction with the *p<sub>x</sub>* and *p<sub>y</sub>* orbitals is at least two orders of magnitude weaker. Hydrogen bound to the symmetric bridging oxygen is bound to Mo in the *y* direction; accordingly, the only significant bonding takes place between the oxygen *p<sub>y</sub>* orbital and the hydrogen *s* orbital. On the other hand, hydrogen over the terminal oxygen is bound at an angle. In this case, the COOP plots reveal approximately equal bonding to the *p<sub>z</sub>* and the *p<sub>x</sub>* orbitals.

#### IV. DISCUSSION

The bonding of the oxygens to Mo in MoO<sub>3</sub> (010) has both ionic and covalent character, with differences in covalent bonding between the different oxygens. The contribution of covalent bonding is evident in the COOP plots between

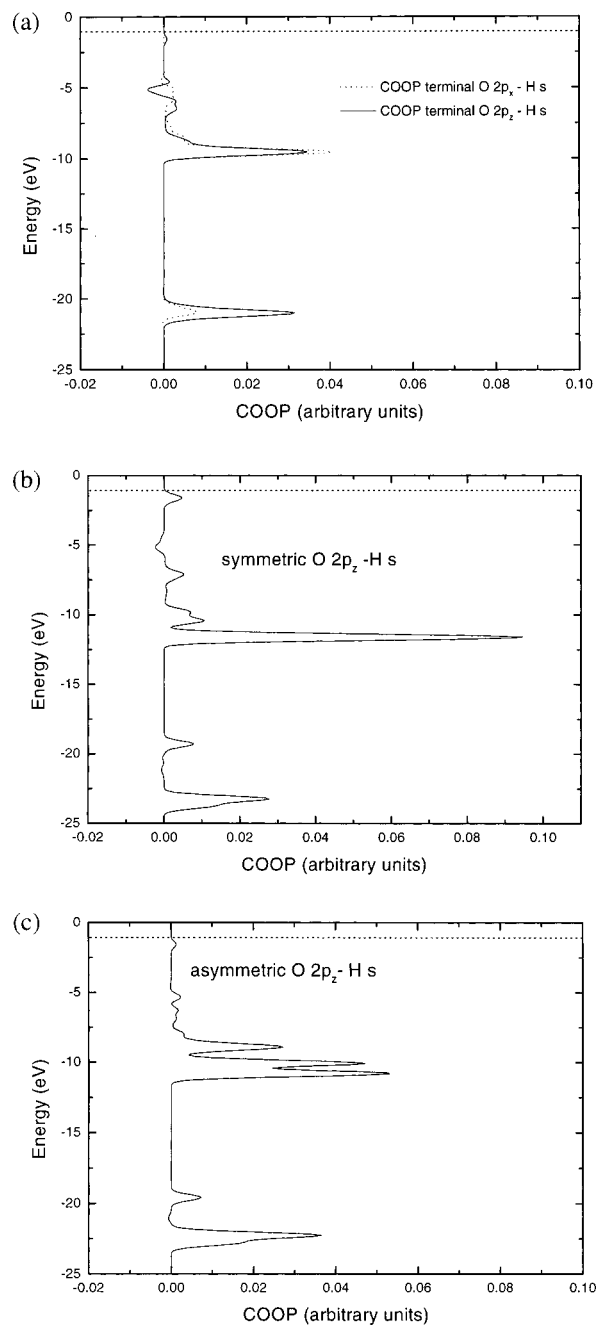


FIG. 6. (a) COOP between hydrogen 1*s* and terminal oxygen 2*p<sub>x</sub>* and 2*p<sub>z</sub>* orbitals, hydrogen adsorbed over terminal oxygen. (b) COOP between hydrogen 1*s* and symmetric bridging oxygen 2*p<sub>z</sub>* orbitals, hydrogen adsorbed over symmetric bridging oxygen. (c) COOP between hydrogen 1*s* and asymmetric bridging oxygen 2*p<sub>z</sub>* orbitals, hydrogen adsorbed over asymmetric bridging oxygen. The dotted line indicates the position of the Fermi level.

the Mo *d* orbitals and the oxygen *p* orbitals (Fig. 4). The sum of the COOP curves up to the Fermi level (OPDOS), while not quantitatively meaningful, reflects the relative amount of covalent bonding present (Table III). The strongest covalent bonding is found in the terminal oxygen, followed by the asymmetric bridging oxygen. This is not surprising, given the relatively short bond lengths of these two oxygen species. The covalent bonding of the terminal oxygen is due to a different orbital interaction than that of the asymmetric bridging; the terminal oxygen bonding is from Mo *d*–O *p*

TABLE III. Total OPDOS of Mo with oxygen.

Type of oxygen	OPDOS Mo 5d–O 2p	OPDOS Mo 6p–O 2p	Total OPDOS
Symmetric bridging	0.06	0.10	0.16
Asymmetric bridging	0.05	0.16	0.21
Terminal	0.21	0.07	0.28

mixing, while the asymmetric bridging oxygen bonding is due to Mo  $p$ –O  $p$  interaction (Figs. 3 and 4). There are also differences in the coordination number in the various oxygen species that may affect the bonding of adsorbates to the surface. The symmetric bridging and asymmetric bridging oxygens are coordinated to more than one Mo atom, while the terminal oxygen is coordinated to only one Mo atom, and is able to form a double bond with the metal atom. This fact has implications for the different chemical properties of the various oxygen species. It has been postulated that the terminal oxygen is the reactive species in the partial oxidation of methane. These calculations support this hypothesis; however, there are several factors relevant to the reaction of larger molecules that have not been taken into account. For example, steric effects need to be considered, because a larger molecule may need to approach the surface at a particular orientation in order for the reaction to occur.

While there have also been several earlier *ab initio* studies of  $\alpha$ -MoO<sub>3</sub> surfaces using both cluster and slab models, none have allowed full relaxation of the surface atoms. Allison and Goddard performed generalized valence bond and configuration interaction calculations on small clusters designed to mimic the various oxygen sites in MoO<sub>3</sub>.<sup>14</sup> They concluded that sites involving di-oxo groups were important for removing hydrogens from methanol. In this study the clusters were small (5 atoms) and Cl was substituted for bridging oxygens. Hence geometry optimization was not possible, and finite-size effects are likely to be important. Michalak *et al.* also used a cluster model to simulate the (010) and (100) surfaces of MoO<sub>3</sub> using density functional theory.<sup>15</sup> They capped the cluster by adding an appropriate number of hydrogens to each edge oxygen, depending on the type of oxygen. Their calculations indicated that the symmetric bridging oxygen was the most highly charged species, with the asymmetric and terminal oxygens demonstrating some covalent bonding, in qualitative agreement with our work. All bond lengths in their cluster were fixed to experimental values, and the capping hydrogens were also fixed at a constant distance. Sautet *et al.* performed an extensive study of  $\alpha$ -MoO<sub>3</sub> (100) with correlated Hartree–Fock methods, calculating the electronic structures of small cluster units as well as the extended surface.<sup>16</sup> They found that the bonding of the various oxygens was predominately ionic in nature, with some covalent bonding for the terminal oxygen. They also tested the adsorption of various small molecules such as H<sub>2</sub>O and CO in order to explain the reactivity of the (100) surface; here again, the MoO<sub>3</sub> surface was not allowed to relax. Hermann *et al.*<sup>17</sup> studied the adsorption of hydrogen using density functional theory on a cluster model of MoO<sub>3</sub> (010), finding that the terminal oxygen site was the most

stable site for hydrogen adsorption. Finally, Corà *et al.*<sup>18</sup> performed a Hartree–Fock study of the bulk MoO<sub>3</sub> structure, relaxing the ionic positions manually to find the lowest energy configuration. In this case the ionic degrees of freedom were relaxed individually, instead of simultaneously as would be done in a full relaxation. In this study it was found that the terminal oxygen was the only oxygen species with any covalent character, while the bridging oxygens were bonded ionically to the molybdenum atom. The interlayer bonding was also examined, and it was found that this bonding was weak in nature and consists of a combination of dispersive and long-range electrostatic interactions.

Our calculation also shows that it may not be possible to consider MoO<sub>3</sub> bonding in terms of oxo groups, as Allison and Goddard have suggested.<sup>14</sup> The oxo groups pointed out by Allison and Goddard refer to a Mo atom bonded with the terminal oxygen and the short bond of the asymmetric oxygen. The authors suggest that this species is a Mo<sub>3</sub> atom with two equivalent, doubly bound oxygens, by correlating bond length to bond strength, since the terminal and asymmetric bridging oxygens have similar bond lengths. This reasoning holds for small molecules, but is not true for extended solids. In fact, the clusters used by Allison and Goddard to model MoO<sub>3</sub> were so small that long-range effects were ignored altogether. For example, the most striking difference between the terminal and asymmetric bridging oxygens is the fact that the bridging oxygen is coordinated to two Mo atoms, while the terminal oxygen is coordinated to only one. Our calculations show that these two oxygen species are not alike. While both the terminal oxygen and the asymmetric bridging oxygen do have covalent character, the orbitals which participate in the bonding are different; for the terminal oxygen, it is the Mo  $d$  orbitals which are important, while for the asymmetric bridging oxygen it is the Mo  $p$  orbitals which contribute to the bonding. Our results are in agreement with those of Papakondylis *et al.*,<sup>16</sup> Michalek *et al.*,<sup>15</sup> and Corà *et al.*<sup>18</sup>

Our calculations of the MoO<sub>3</sub> surface with hydrogen adsorbed demonstrate the importance of ionic relaxation in investigating the chemical properties of a surface. Hermann *et al.* studied hydrogen adsorption on clusters designed to mimic the MoO<sub>3</sub> (010) surface.<sup>17</sup> In their studies only the hydrogen-cluster distance was optimized to obtain the minimum-energy configuration. Their results indicated that the most stable binding site for hydrogen was over the terminal oxygen, consistent with our results. The fact that relaxation of the cluster was not considered could change the calculated adsorption energy substantially. Full relaxation of the surface in adsorption studies is crucial because it allows the atoms to change position so as to accommodate the adsorbate. Moreover, relaxation also allows important electronic changes to take place; for example, a transition from a double bond to a single bond in the terminal oxygen as a result of hydrogen adsorption is accompanied by an analogous change in the bond length.

The bonding of hydrogen to the different oxygen species can be explained by examining the changes in covalent bonding that occur when the oxide surface forms a bond with the hydrogen. For example, as a result of hydrogen binding

to the terminal oxygen the Mo–O bond is lengthened by 0.3 Å. The change in Mo–O bonding is clearly reflected in the OPDOS, where it is evident that there is a loss of covalent bonding between the Mo and the terminal oxygen. The value for the integrated COOP (OPDOS) shows a decrease in the total covalent bonding between these two atoms, from 0.2 to 0.1. Similarly, for hydrogen adsorbed over the symmetric bridging oxygen, there is a surface relaxation in which the two Mo–O sheets which make up the slab move apart by 0.2 Å. The symmetric bridging oxygen cannot support four bonds, and in order to bind to the hydrogen the oxygen is forced to weaken a bond to one of the surrounding Mo atoms. The bond that is weakened is to the Mo that is farthest away. The COOP also shows this effect clearly; the OPDOS decreases from 0.03 to 0.02. Interestingly, the effect of hydrogen over the asymmetric bridging oxygen is to make the two Mo–O bonds more symmetric. The oxygen is now threefold coordinated, similar to the symmetric bridging oxygen, and thus behaves analogously with the oxygen bonded symmetrically between two Mo atoms. The bonding of hydrogen to the various oxygens involves covalent interaction of the hydrogen  $1s$  orbital with the oxygen  $2p$  orbitals. This interaction is predominantly bonding in nature, because the strong overlap of the hydrogen and oxygen orbitals push the antibonding levels above the Fermi level. One aspect of the hydrogen bonding is that over the asymmetric bridging oxygen, hydrogen is bound directly on top, whereas in the terminal case hydrogen is bound at an angle. This can be explained by a COOP analysis of the O  $2p$ –H  $1s$  orbital interaction, decomposed into the separate  $p$  orbitals (Fig. 6). Hydrogen interacts with the bridging oxygens only through the  $p_z$  orbitals; there is little overlap with the  $p_x$  or  $p_y$  orbitals. In the case of the terminal oxygen, one would expect from a simple orbital analysis that the terminal oxygen would be  $sp^2$  hybridized, and thus would have orbitals in a trigonal planar configuration, mixing  $2s$ ,  $2p_x$ , and  $2p_y$ . The COOP plot [Fig. 6(a)] confirms this prediction, showing almost equal amounts of covalent bonding between the hydrogen  $1s$  orbital and the terminal oxygen  $2p_x$  and  $2p_y$  orbitals.

We now examine the relative ordering of hydrogen adsorption energies for the different oxygen sites. The terminal and asymmetric bridging sites bind hydrogen more strongly compared to the symmetric bridging site, which is more than 0.3 eV less stable. The reason for this result is that for hydrogen to bind to the symmetric bridging oxygen, a Mo–O bond must be weakened, as opposed to the other oxygen sites. Surface relaxation must be included in the calculation; otherwise these effects would not be observed. In fact, the frozen surface calculation results in the symmetric bridging

oxygen site binding hydrogen more strongly than the asymmetric bridging oxygen, because without surface relaxation important electronic factors such as bond weakening and bond breaking are not taken into account.

## V. CONCLUSIONS

The present calculations of the  $\alpha$ -MoO<sub>3</sub> (010) surface demonstrate the ability of the density-functional, pseudopotential, plane-wave methodology to accurately describe bond lengths and bonding character in this mixed ionic-covalent system. The calculated bond lengths are all within 1.1% of x-ray crystallographic measurements. The analysis of the bonding reveals that the interaction between Mo and oxygen is a combination of ionic and covalent bonding. Differences in bonding between the various types of oxygen can be traced to differences in the amount of covalent bonding present. The terminal oxygen has more covalent character than either of the bridging oxygens, which may manifest itself in differences in reactivity. Calculations of hydrogen adsorbed on MoO<sub>3</sub> show that the most stable binding site is the terminal bridging oxygen. Furthermore, it is important to include surface relaxation when considering the bonding of an adsorbate to an oxide surface; failure to do so may result in qualitatively incorrect results.

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