PHYSICAL REVIEW B VOLUME 62, NUMBER 15 15 OCTOBER 2000-I

Influence of intermolecular hydrogen bonding on water dissociation at the MgO(001) surface

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(Received 14 March 2000)

The adsorption of water on the MgO(001) surface is studied by using density-functional theory calculations within the generalized gradient approximation. Our calculations show that coupled three and four water molecules are partly dissociated, indicating that the intermolecular hydrogen bonding plays an important role in water dissociation on MgO(001). Especially, four water molecules are found to be significantly stabilized due to the increase in the number of the intermolecular hydrogen bonds. This hydrogen-bonding unit can explain experimental observations of the $c(4\times2)$ phase and its transition to the $p(3\times2)$ phase composed of three water molecules.

The interaction of water with oxide surfaces is interesting because of its importance for understanding various fundamental phenomena such as heterogeneous catalysis, corrosion, ground-water contaminants, and atmospheric chemistry.[1] As a model system, the adsorption of water on the MgO(001) surface has been intensively studied both experimentally[2–8] and theoretically.[9–16] Despite many studies, there has been a controversy concerning whether the type of water adsorption on MgO(001) is molecular or dissociative. Earlier theoretical calculations[9–12] predicted that water dissociation on a clean MgO(001) surface is energetically unfavorable, but at a defective surface the dissociation can be stabilized. Thus, the vibrational spectra of the hydroxyl group by infrared spectroscopy[4,5] were tentatively ascribed to water dissociation at steps and defects.

However, unlike earlier experiments[2–4] performed on powdered MgO substrates containing various surface defects, recent experiments[5–8] determined the structure of water adsorbed on a single-crystal MgO(001) surface. A spot profile analysis low-energy electron diffraction (SPA-LEED) experiment[5] showed that the adsorbed water molecules form a $c(4\times2)$ phase at about 150 K. Subsequently, LEED and helium-atom scattering (HAS) experiments[6] also showed that the water adsorption at $T=100$–180 K forms a layer with the $c(4\times2)$ phase and annealing at $T=185$–221 K leads to the formation of a new ordered phase of the $p(3\times2)$ symmetry. The experimental observations of the $p(3\times2)$ phase stimulated theorists to determine its atomic structure. Recent two first-principles calculations by Giordano, Goniakowski, and Suzanne[15] and by Odelius[16] reported that the $p(3\times2)$ water monolayer contains H_2O in both molecular and dissociated forms. However, there is no theoretical study for the low-temperature phase of $c(4\times2)$, and its phase transition to $p(3\times2)$ as well. Thus, an understanding of the water adsorption on MgO(001) is still lacking.

In this paper we study the energetical and geometrical properties of water molecules adsorbed on MgO(001) by means of the density-functional theory[17] within the generalized gradient approximation (GGA).[18] We find that the dissociation of either a water molecule or a water dimer is energetically unfavored, but in the presence of three or four water molecules, the mixture of molecular and dissociative adsorption is stabilized by the intermolecular hydrogen bonding. Especially, four water molecules are more stable than three water molecules which are the basic unit of the $p(3\times2)$ water monolayer in the previous first-principles calculations.[15,16] This higher stability of four water molecules is likely to form a well-ordered island with the $c(4\times2)$ structure, supporting the experimental observation of the $c(4\times2)$ phase at low temperature. With the hydrogen-bonding units of three and four water molecules, we will explain the phase transition from $c(4\times2)$ to $p(3\times2)$ accompanied by water desorption.[6,7]

Our total-energy calculations have been performed using the plane-wave-basis pseudopotential method within the GGA. We use the exchange-correlation functional of Perdew, Burke, and Ernzerhof[18] for the GGA calculations. The Mg and H atoms are described by the norm-conserving pseudopotentials of Troullier and Martins[19] and the O atom is described by the ultrasoft pseudopotential of Vanderbilt.[21] The MgO(001) surface is modeled using a periodic slab geometry consisting of three atomic layers and a vacuum region of seven such layers.[20] Water molecules are adsorbed on both sides of the slab. For the $c(4\times2)$ structure, we employ the equivalent $p(4\times2)$ cell whose surface area is twice as large as that of the $c(4\times2)$ cell. The electronic wave functions are expanded in a plane-wave basis set using a cutoff energy of 25 Ry, and the electron density is obtained from the wave functions calculated at four **k** points in the surface Brillouin zone of the $p(3\times2)$ and $p(4\times2)$ unit cells.[22] Here, the positions of all atoms, except the innermost one MgO layer held at their theoretical bulk positions ($a_0=4.23$ Å), are allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components are less than 0.02 eV/Å.

We first determine the atomic structure of water molecules adsorbed on MgO(001) with increasing number of molecules within the $p(3\times2)$ cell. The top and side views of the optimized structures of one, two, three, and four water molecules, corresponding to coverage $\theta=1/6$, 1/3, 1/2, and 2/3 ML, are given in Fig. 1, together with the calculated adsorption energy. We find that the adsorption energy increases with increasing coverage, indicating the attractive interaction between the adsorbed water molecules. Note that in

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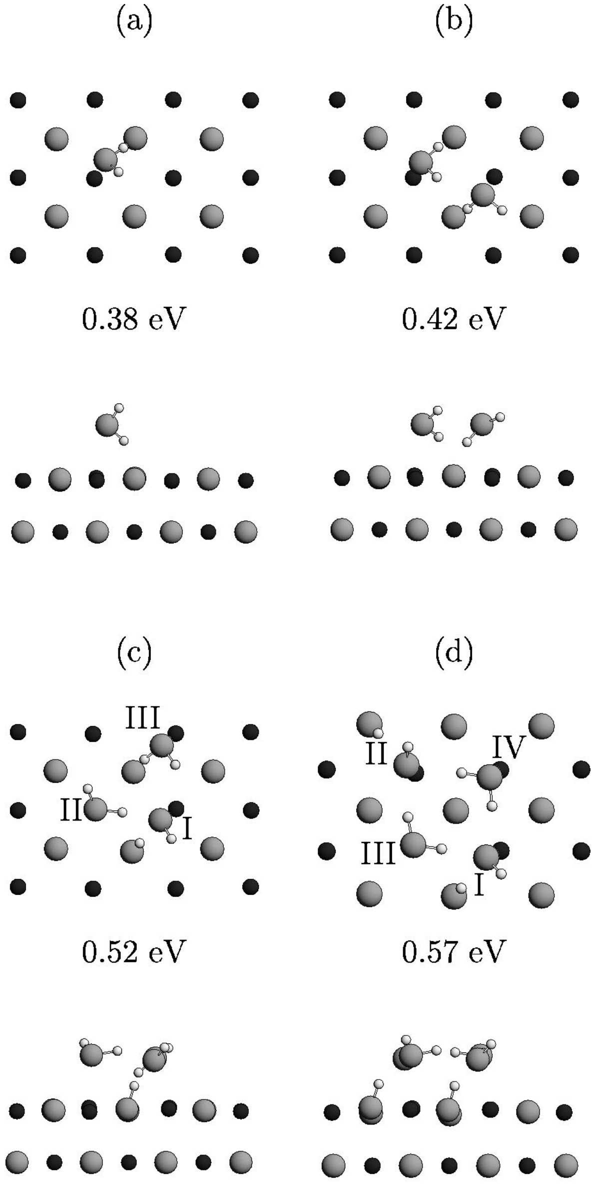

FIG. 1. Top and side views of the optimized atomic structures of water molecules on MgO(001): (a) one, (b) two, (c) three, and (d) four water molecules. The large, medium, and small circles represent O, Mg, and H atoms, respectively. In the side view of (d), one OH bond of the molecule III (IV) directing inward (outward) the page is hidden. The adsorption energy for each structure is given.

three [Fig. 1(c)] and four [Fig. 1(d)] water molecules one and two molecules are dissociated to form hydroxyls, respectively. This *mixed molecular and dissociative* adsorption is highly stabilized by the hydrogen-bonding interaction between water molecules and hydroxyls. The adsorption energies of three and four water molecules are much larger than those of the simple molecular adsorptions of one and two water molecules (see Fig. 1). Here, the mixed molecular and dissociative adsorption of four water molecules are most favorable because of the increase in number of the intermolecular hydrogen bonds.

As shown in Fig. 1(a), an isolated water molecule adsorbs molecularly on MgO(001), where one hydrogen atom points toward the neighboring surface oxygen and the other hydrogen atom points away from the surface. This geometry of the isolated water molecule agrees well with the previous result of Langel and Parrinello.[11] Such molecular geometry is also preserved in two water molecules [see Fig. 1(b)]. The atomic positions of one and two water molecules are given in Table I. In three water molecules, there are three types of molecules [denoted I, II, and III in Fig. 1(c)]. Only the molecule I dissociates, transferring the hydrogen to the surface oxygen; the OH bonds of the molecule II are nearly parallel to the MgO surface; the geometry of the molecule III is similar to that of an isolated water molecule. These features of three water molecules are very close to those in the $p(3\times2)$ water monolayer obtained by Giordano, Goniakowski, and Suzanne.[15] On the other hand, in the case of four water molecules [Fig. 1(d)] the OH bonds of the molecules III and IV are nearly parallel to the MgO surface and point toward the dissociated molecules I and II as a consequence of the intermolecular hydrogen bonding. This parallel geometry of the OH bonds accords with the analysis from the Fourier-transform infrared spectra[5] of the $c(4\times2)$ phase, in which the water molecules lie flat on the surface with a strong hydrogen bonding between the adsorbates.

TABLE I. Calculated atomic positions of one [Fig. 1(a)] and two [Fig. 1(b)] water molecules relative to Mg atom. Here the Mg atom is referred to as the one just below the corresponding water molecule. The positions (x,y,z) are given in Å along the [110], $[\bar{1}10]$, and [001] directions, respectively.

	Atom	One water molecule	Two water molecules
H_2O (I)	O	(0.426,0.723,2.110)	(0.307,0.592,2.067)
	H	(0.924,0.264,2.822)	(0.920,0.042,2.620)
	H	(1.115,1.201,1.504)	(0.961,1.191,1.564)
H_2O (II)	O		$(-0.434,-0.730,2.078)$
	H		$(0.306,-1.317,2.357)$
	H		$(-1.025,-1.265,1.351)$

To examine why the water dissociation is favored over the molecular adsorption, we calculate the energy profile of the optimized structures with respect to the given bond length $d_{H_t-O_s}$ between the transferred hydrogen (H_t) and the neighboring surface oxygen (O_s). The calculated adsorption energies for one, two, and three water molecules as a function of $d_{H_t-O_s}$ are shown in Fig. 2. We find that in both one and two water molecules the adsorption energy monotonically decreases in magnitude with decreasing $d_{H_t-O_s}$, showing that water dissociation cannot be stabilized. However, in three water molecules the dissociation of the molecule I is stabilized at $d_{H_t-O_s}=1.05$ Å over the molecular adsorption. Moreover, in the case of three water molecules water dissociation occurs barrierless. Our results for the energetics of water dissociation are quite different from those obtained from the molecular dynamics study of Odelius,[16] where the dissociative adsorption can be stabilized as a metastable state even in one water molecule and the mixed molecular and dissociative adsorption is strongly favored in two water molecules over the molecular adsorption,[23] but the barrier for dissociation was too high to occur spontaneously in his simulation.

Next, we determine the atomic structures of the $p(3\times2)$ and $c(4\times2)$ water monolayers. Here we model the

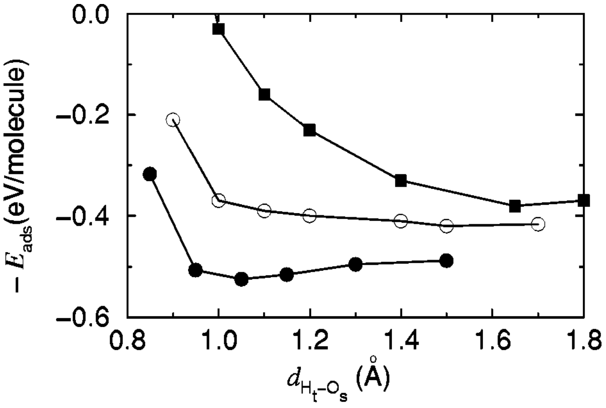

FIG. 2. Adsorption energies of water molecules on MgO(001) as a function of the bond length between the transferred hydrogen and surface oxygen. The filled square, open circle, and filled circle represent the results for one, two, and three water molecules, respectively.

former by arranging a pair of the three water molecules [Fig. 1(c)] in the unit cell with the glide plane symmetry, in accordance with the experimental observation,[6,8] and the latter by arranging the four water molecules [Fig. 1(d)] with a $c(4\times2)$ symmetry. The top views of the optimized structures of the $p(3\times2)$ and $c(4\times2)$ water monolayers are given in Fig. 3. Comparing the geometry of the $p(3\times2)$ water monolayer [Fig. 3(a)] with the three water molecules [Fig. 1(c)], we see that the molecule III changes the direction of the OH bonds, pointing toward the neighboring molecules. The molecule III converts to the type of molecule II by the intermolecular hydrogen bonding. Our calculated adsorption energy for the $p(3\times2)$ water monolayer ($E_{\mathrm{ads}}=0.59$ eV) agrees well with the previous theoretical result of Giordano, Goniakowski, and Suzanne[15] (0.60 eV), but deviates largely from that calculated by Odelius[16] (0.48 eV). This deviation is too large to ascribe the reason to the different calculational parameters.[24] In fact, both previous calculations[15,16] used the similar calculational parameters such as the *ab initio* norm-conserving pseudopotentials and the GGA functionals of Becke.[25] Thus, we doubt the energetics of the $p(3\times2)$ water monolayer calculated by Odelius,[16] together with the energetics of water dissociation in two water molecules.[23] For the $c(4\times2)$ water monolayer we find a slightly larger adsorption energy ($E_{\mathrm{ads}}=0.61$ eV) compared to that of the $p(3\times2)$ one. Note that there is a large discrepancy in the magnitude of the adsorption energy between theories and experiment (see Table II), demanding further detailed investigations from both sides.

According to the LEED and HAS experiments,[5–7] at $T=140$ K, the superstructure peaks corresponding to the $c(4\times2)$ phase start to grow quickly only when the water coverage exceeds 0.7 ML,[5,7] while at high temperatures ($T=185$–210 K) those for the $p(3\times2)$ phase do not appear up to the water coverage of about 0.4 ML.[6] These experimental observations imply the existence of the critical coverage above which large and well-ordered islands of water with the $c(4\times2)$ and $p(3\times2)$ symmetries are formed. Considering that the above observed critical coverages are close to the coverages of the three and four water molecules we considered, we believe that, although the kinetics of such water molecules is beyond the present study, the three and four water molecules may easily aggregate to form well-ordered islands of the $p(3\times2)$ and $c(4\times2)$ phases, respectively. This aggregation of water molecules is favored by thermodynamics: e.g., the calculated adsorption energy for monolayers is larger than those of the isolated three and four water molecules. It was also observed from the HAS measurements[6,7] that the phase transition from $c(4\times2)$ to $p(3\times2)$ is accompanied by the desorption of water mol-

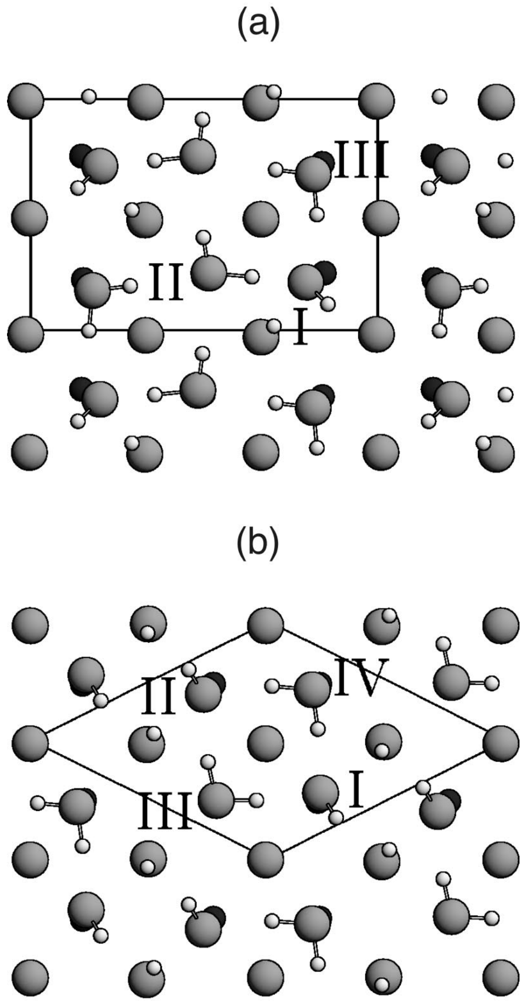

FIG. 3. Top views of the optimized structures of the $p(3\times2)$ (a) and $c(4\times2)$ (b) water mono-layers on MgO(001).

TABLE II. Calculated adsorption energy for the water monolayer adsorbed on MgO(001) in comparison with previous theoretical and experimental data.

	Structure	E_{ads} (eV)
Previous theory[a]	$p(3\times2)$	0.60
Previous theory[b]	$p(3\times2)$	0.48
This work [Fig. 3(a)]	$p(3\times2)$	0.59
This work [Fig. 3(b)]	$c(4\times2)$	0.61
Experiment[c]	$p(3\times2)$	0.88

[a] Reference 15 (Giordano, Goniakowski, and Suzanne, 1998).
[b] Reference 16 (Odelius, 1999).
[c] Reference 6 (Ferry *et al.*, 1996).

ecules from the surface, and further the $c(4\times2)$ phase cannot be obtained through the cooling of the $p(3\times2)$ phase without additional water supply. Based on the experimental observation of water desorption during the process of the phase transition and assuming that islands of the $p(3\times2)$ and $c(4\times2)$ phases are composed of three and four water molecules, respectively, we speculate that the $c(4\times2)$ phase might be transformed into a $p(3\times2)$ phase by the desorption of one water molecule out of four water molecules in the $c(4\times2)$ phase. Here, we note that the ''local'' coverages of both phases are the same, corresponding to one water molecule per surface Mg-O unit, but the total coverage after the phase transition is reduced by the factor of 1/4 because of water desorption.

In conclusion, we have performed first-principles calculations for the adsorption of water molecules on MgO(001) with increasing water coverage. We found that the mixed molecular and dissociative adsorption of three and four water molecules is highly stabilized as a consequence of the increased hydrogen bonds between water molecules and hydroxyls. With these hydrogen-bonding molecule units we tentatively interpret experimental observations for the superstructure phase of $p(3\times2)$ and $c(4\times2)$, and their phase transition accompanied by water desorption as well.

This work was supported by Creative Research Initiatives of the Korean Ministry of Science and Technology.

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[22] The employed plane-wave-basis cutoff (E_{pw}), **k** points (N_k), and slab thickness yield well-converged results for the adsorbed water geometries and energetics. Additional calculations with $E_{\mathrm{pw}}=30$ Ry, $N_k=8$, and five slab thickness of MgO substrate show little changes of the OH bond lengths and the relative stabilities of the energetics (by less than 0.01 eV).

[23] In Ref. 16 Odelius found the adsorption energy for the mixed molecular and dissociative adsorption of two water molecules to be 0.55 eV, which is much larger than his value for the $p(3\times2)$ water monolayer (0.48 eV). This higher stability of two water molecules is questionable because the intermolecular hydrogen bonding between water molecules increases the stability of water adsorption on MgO(001) with increasing coverage.

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