Partial Dissociation of Water Molecules in the (3×2) Water Monolayer Deposited on the MgO (100) Surface

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(Received 27 March 1998)

Using the *ab initio* total energy method based on the gradient-corrected local density approximation we have modeled the experimentally observed (3×2) water monolayer on the MgO (100) surface. The lateral interactions between the adsorbed water molecules, the formation of hydrogen bonds, and the resulting strong dimerization of the adsorbate promote the dissociation of two out of six water molecules in the surface unit cell. Although, on the theoretical grounds, water dissociation on a defective MgO surface has been already reported, this is the first theoretical evidence of water dissociation on the perfect MgO (100) surface. [S0031-9007(98)06827-6]

PACS numbers: 68.55.Jk, 82.65.Pa

The mechanism of water adsorption on oxide surfaces has been the subject of many studies owing to its importance for understanding numerous fundamental phenomena such as heterogeneous catalysis, corrosion, or passivation. Water at oxide surfaces is also a key phenomenon for modeling of earth subsurface hydrodynamics. As a model system, water on the MgO (100) surface, has been subject to intensive theoretical studies [1–8]. The general conclusion is that water adsorbs molecularly on the perfect (100) surface, dissociative adsorption being possible only on selected surface defects such as steps, kinks, or vacancies. Recent helium atom scattering (HAS) and LEED experiments on well-characterized uniform MgO single crystal surfaces have shown the existence of an ordered $p(3 \times 2)$ water monolayer structure [9,10]. Fourier transformed infrared spectroscopy (FTIR) studies performed on this structure show three sharp absorption bands at 3672, 3626, and 3513 cm^{-1} [11]. They were tentatively ascribed to isolated molecules adsorbed in the molecular form on terraces and dissociatively on surface steps. This, however, appears to be incoherent with the HAS and LEED results that clearly show the (3×2) pattern. The only existing theoretical evidence concerning the (3×2) phase is the semiempirical molecular dynamics simulation [10] in which the water molecules are found to physisorb flat on top of surface cation sites, the hydrogen atoms point approximately along the Mg rows forming weak hydrogen bonds. Although the experimentally determined adsorption energy is relatively high, none of the results of the semiempirical model show chemical bonding to the substrate.

Here, using an *ab initio* approach, we show that in the (3×2) water monolayer deposited on the MgO (100) surface, due to interaction between the adsorbed molecules some of them dissociate. Since the dissociation is conditioned by the reconstruction of the monolayer, it was not found for adsorption of a single water molecule, nor for an unreconstructed (1×1) monolayer [6]. On the other hand,

since the semiempirical calculations [10] cannot account for deprotonation of water molecules, no surface dissociation was found by this method. Our results show, for the first time in the case of an experimentally observed structure, the influence of the cooperative interactions between adsorbate in a dense monolayer on their chemical reactivity towards an oxide surface.

In the present study we have used the density functional based pseudopotential method [12] with the gradient-corrected (GC) Becke-Perdew exchange-correlation potential [13]. As was already pointed by several authors, the GC extension is crucial for the accurate treatment of the hydrogen bonds, and its inclusion leads to a successful description of, e.g., structure of water [14], ice [15], and surface adsorption or dissociation of water [16–18]. All results presented in this paper issue from steepest descent geometry optimization. The search for energy minimum was stopped when atomic forces are less than 0.005 eV/Å. We have used first-principles Trouiller-Martins [19] pseudopotentials in the Kleinman-Bylander representation [20] that have already proven their adequacy for description of perfect and defective MgO (100) surfaces [21]. Results of additional tests on a free water molecule and a free water dimer are summarized and compared to the experimental data in Table I. They remain perfectly consistent with the existing gradient-corrected LDA results [15,22]. In order to further validate our approach, we have considered adsorption of an isolated water molecule on the MgO (100) surface. The results are summarized in Table II. In perfect agreement with the authors of Ref. (6), we find that an isolated water molecule adsorbs on top of a surface cation, does not dissociate upon the adsorption, and forms a hydrogen bond with the neighboring surface oxygen.

For the study of the water monolayer, following the experimental findings, we have considered a (3×2) MgO surface unit cell, containing six adsorbed water molecules. Three layer thick (100) MgO slab and a single Γ point

TABLE I. Calculated and experimental results for a free water molecule and a free water dimer.

		Theory	Expt.[a]
Free H_2O	O-H bond length (Å)	0.97	0.96
	HOH bond angle (deg)	104.9	104.5
H_2O dimer	O-O distance (Å)	2.85	2.98
	Formation energy (kJ/mol)	18	23

[a]Ref. [23]

were used in the calculations. Starting from the atomic configuration issued from the semiempirical calculations [10] we have optimized the positions of all atoms of the deposited water monolayer and of the surface layer of MgO. The final atomic configuration obtained in the structure-optimization run is depicted in Fig. 1 and summarized in Tables II and III. We find, in agreement with the experimental data, that the (3×2) cell has the $p1g1$ glide plane symmetry. The monolayer contains three inequivalent types of adsorbed water molecules, denoted I, II, and III, as indicated in Fig. 1.

The water molecules of type I dissociate, transferring their proton (denoted Ia in Fig. 1) to the neighboring surface oxygen sites. This is especially well seen in the side view in Fig. 1b. It should be noticed that the transfer occurs along a hydrogen bond between the water molecule I and the neighbor surface oxygen and that the dissociation does not break this bond. This is reflected by a short distance between the corresponding oxygen atoms (2.52 Å). The water molecules of type II adsorb nearly parallel to the MgO surface. They shift horizontally from on top of cation sites and approach closely the water molecules of type I. The short oxygen-oxygen distance between these two molecules (2.50 Å) and the orientation of the $O_{II}H_{IIa}$ group indicate the existence of a hydrogen bond. Although molecules of type I and II form what can be regarded as a water dimer, the presence of the substrate induces an important modification of its properties reflected by the shortening of the oxygen-oxygen distance (as compared to 2.85 Å for a free water dimer) and dimerization-induced proton transfer towards the surface oxygen site.

TABLE II. Calculated and experimental results for the isolated water molecule and for the (3×2) water monolayer adsorbed on the MgO (100) surface. Distances correspond to the vertical separation between the oxygen atom of adsorbed water molecule and the surface. Results for the monolayer correspond to an average value per molecule.

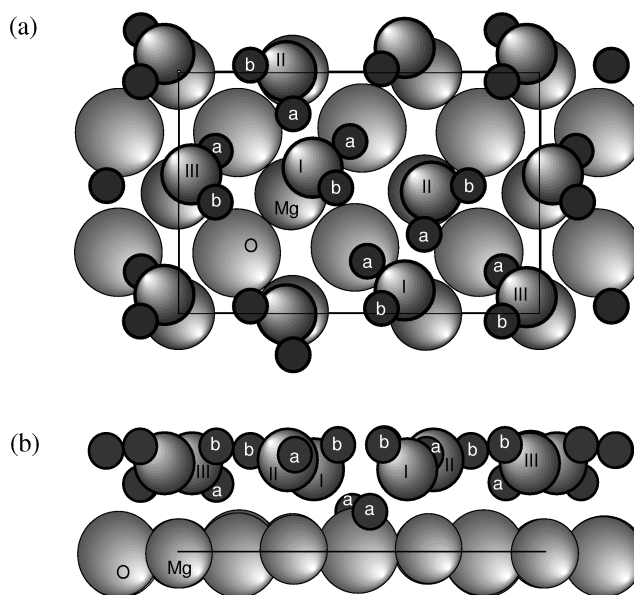|		Theory	Expt.[a]
Isolated mol.	Molecule-surface distance (Å)	2.10	
	E_{ads} (kJ/mol)	33	50 ± 10
Monolayer	Layer-surface distance (Å)	2.08	2.11
	E_{ads} (kJ/mol)	58	85 ± 2

[a]Ref. [10]

FIG. 1. Calculated geometry of the (3×2) reconstructed water monolayer on the MgO (100) surface. Three inequivalent types of water molecules are denoted with I, II, and III. (a) View from above showing the dimerization between molecules of type I and II; (b) side view showing the transfer of protons Ia to the surface oxygen sites.

This situation is similar to that reported already for the water adsorption on the (110) surface of TiO_2. In that case, an enhanced mobility of the hydrogen atom along water-surface hydrogen bond leads to a coexistence of molecular and dissociated water, stabilized by a mutual hydrogen bond [17]. Finally, the water molecules of type III adsorb in a way which is very similar to that of an isolated water molecule, clearly forming a hydrogen bond with the neighboring surface oxygen. As is the case for an isolated water molecule, the hydrogen participating to this hydrogen bond (H_{IIIa}) is not transferred to the surface oxygen.

Upon adsorption, the OH bonds of water molecules became inequivalent. This is reflected by changes of their length with respect to $d_{OH} = 0.97$ Å for a free water molecule. The bond lengths calculated for water molecules of three different types are reported in Table III. For the three types of water molecules one of two hydrogens participates weakly to the interactions with the neighbors and the corresponding OH bond length

TABLE III. Calculated lengths of OH bonds (in Å) for the (3×2) water monolayer adsorbed on the MgO (100) surface.

Molecule I	$O_{surface}$-H_{Ia}	1.03
	O-H_{Ib}	0.96
Molecule II	O-H_{IIa}	1.03
	O-H_{IIb}	0.97
Molecule III	O-H_{IIIa}	1.00
	O-H_{IIIb}	0.97

remains practically unchanged as compared to the free molecule. These hydrogens are denoted as (b) in Fig. 1. On the other hand, remaining OH bonds [with hydrogens denoted as (a)] are modified differently for different types of water molecules. In the case of water of type I, the hydrogen Ia is transferred to the surface oxygen, forming a surface OH group. The hydrogen IIa participates to the hydrogen bond between molecules I and II. Finally, the hydrogen IIIa participates to the hydrogen bond with a surface oxygen. Per unit cell, we find thus six OH bonds similar to those in a free water molecule ($d_{OH} = 0.97$ Å), two slightly longer ($d_{OH} = 1.00$ Å), and four still longer ($d_{OH} = 1.03$ Å).

The present findings reconcile the majority of existing experimental results and give a new, coherent picture of water adsorption on the MgO surface. On the one hand, strong dimerization and partial dissociation of water molecules in the (3×2) layer considerably increases the mean adsorption energy. In agreement with the experimental data we find that the adsorption energy calculated for the molecule in the monolayer is nearly twice as large as that of an isolated molecule (see Table II) and approaches the adsorption energies calculated for dissociative adsorption of water on the step edges [6].

On the other hand, the hydrogens transferred to the MgO surface upon the dissociation form surface OH groups. The existence of this kind of group was considered as conditioned by the presence of surface defects. Our results show that the surface OH groups can also exist on a perfect (100) surface and suggest that the sharp band observed in FTIR experiments [11] may arise from vibrations of water dissociated on the defectless surface. A molecular-dynamics study of temperature stability of the calculated structure and water desorption modes together with an evaluation of vibrational frequencies of water in the (3×2) monolayer and the comparison with FTIR experiments will be reported in the forthcoming paper.

In conclusion, we have studied the experimentally observed (3×2) monolayer of water on the perfect MgO (100) surface. We find that as a consequence of dimerization between the molecules in the deposited monolayer two of six water molecules in the surface unit cell dissociate by transferring their protons along hydrogen bonds towards surface oxygen sites. To the best of our knowledge this is the first time that the water dissociation on the perfect MgO (100) surface is reported. We believe that the present results shed a new light on a long lasting question of properties of water-covered MgO and on the role of cooperative lateral interactions on adsorption behaviors.

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