

Mixed Molecular and Dissociative Water Adsorption on MgO[100]

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First principles molecular dynamics (MD) simulations, of water adsorption on the MgO[100] surface, was performed to determine the molecular structure and chemical nature of the adsorbed water at varying coverage. Dissociative adsorption was stabilized by hydrogen bond donation from neighboring water molecules. The dissociation barrier had a strong dependence on coverage. Spontaneous dissociation was observed in picosecond MD simulations above 1/2 monolayer (ML) coverage. Ordered structures with $c[3 \times 2]$ symmetry were examined at 2/3 and 1 ML coverage. The ordered $c[3 \times 2]$ phase consisted of a mixture of dissociated and molecular adsorbed molecules. [S0031-9007(99)09103-6]

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Adsorption of water on a surface influences both the surface and its interaction with other adsorbants and reactants. Thus, understanding the chemistry of the water/oxide interface is essential for the description of surface phenomena in geology, atmospheric chemistry, environmental protection, corrosion, gas sensors, and heterogeneous catalysis [1–3]. In order to build up an understanding it is necessary to study the system at a microscopic level. One of the most basic questions to ask when studying adsorption on surfaces is whether the molecules adsorb molecularly or dissociatively. In this Letter, I will try to show how this very basic question is linked to the more complex and perhaps more interesting question of how the presence of water influences the adsorption of other species on the magnesium oxide surface. The water adsorption was studied at varying coverage, and the barrier for dissociation was strongly dependent on the coverage. Also, the structure and coverage of an ordered phase of water on MgO[100] was determined by *ab initio* molecular dynamics (MD) simulations. The effect of surface hydration has direct consequences for the function of the MgO[100] surface in catalysis [3], for the dissolution of the MgO[100] surface [4], and for the structure of water at near monolayer (ML) coverage [5]. Magnesium oxide has a high affinity for water and is both of general interest as an easily produced prototype oxide surface and of particular interest as a basic catalyst with good mechanical and thermal properties [2,3].

In the literature, there are different opinions about whether the adsorption on MgO is molecular or dissociative [6]. Experimentally, the vibrational signatures of the hydroxyl group and the water molecule has been used to rationalize ir data [7,8]. The presence of hydroxyl groups on MgO is well documented, but although MgO[100] is the most stable surface [2], there is no compelling evidence that the signals assigned to hydroxyl groups are associated with the perfect MgO[100] surface. Even in carefully controlled ultrahigh vacuum experiments the difficulties with preparation and characterization of the experimental surface [3] leave the results open to interpretation. The lack of signals for the O-H bond

in reflection absorption infrared spectroscopy shows that there are no OH groups normal to the MgO[100] surface [5]. This has been interpreted as evidence that the adsorption cannot be dissociative, since the hydroxyl groups would stand straight up from the surface, and that the molecules are lying in the plane. In theoretical studies, different molecular vibrations have been assigned to interpret the experimental data, depending on which adsorption model has been proposed [6,9,10]. However, the theoretical studies, which potentially contain highly accurate molecular information, are limited by a severe size-accuracy trade-off. Isolated water molecules have been shown to adsorb molecularly at the perfect MgO[100] surface and dissociatively at steps and defects [9,10]. Higher coverage, where the water interaction is significant, has been examined for systems with severe geometrical constraints, with periodic Hartree-Fock [11] and density functional [12] techniques, or with model potentials [6,13–15]. While finishing the work, it came to my attention that there was a new *ab initio* treatment of the water interaction on the MgO[100] surface [16], which allowed for both molecular and dissociative adsorption of water to occur on the surface. (Through geometry optimizations starting from semiempirical results, the authors found that the $c[3 \times 2]$ monolayer involves partial dissociation of the water molecules, which is in good agreement with the results presented in this paper.) In temperature programmed desorption experiments [1], two different ordered phases in thin films of water on the MgO[100] surface has been observed with low energy electron diffraction (LEED) and helium atom scattering (HAS) [5,17]; at low temperatures (<180 K) a phase of $c[4 \times 2]$ symmetry, and in the interval (180–220 K) a phase with $c[3 \times 2]$ symmetry. Two different coverages have been suggested for the $c[3 \times 2]$ phase [5,18].

In the present study, the Car-Parrinello technique [19,20] made it possible to examine the adsorption with both full geometry optimizations and *ab initio* MD simulations, in combination with analysis of the electronic configuration. The calculations [21] were performed

within the density functional framework [22], with gradient corrections (B-LYP) [23,24] to the local density approximation [22]. This level of description has proven very reliable in studies ranging from material science to life sciences [20]. Deuterated water made it possible to use a longer time step. A fictitious electron mass of 1000 au, cf. the Car-Parrinello scheme [19], and a time step of 0.17 fs have been used in the integration of the equations of motion. The sampling of the Brillouin zone was restricted to the Γ point. The Kohn-Sham orbitals have been expanded in plane waves up to an energy cutoff of 70 Ry, giving a good description of the valence in combination with the *ab initio* norm conserving pseudopotentials. The same framework has previously been employed to study the adsorption of isolated water molecules on MgO [9,10] and water adsorption at monolayer coverage on the mica surface [25]. The MgO crystal has a simple rock-salt structure with a lattice constant of 4.21 Å [26]. The B-LYP functional, which is known to overestimate distances, resulted in a lattice constant of 4.27 Å for bulk MgO, but the results were insensitive to small variations in the lattice constant. In the calculations, the MgO[100] surface is modeled by a three-layer-thick slab in periodic boundary conditions, using the calculated lattice constant. Full geometry optimization on the clean surface resulted in an inward relaxation and a rumpling of the slab of 2%, where the cations are more contracted than the anions, which is somewhat larger than in previous calculations [9,12,27]. Overall, however, the smoothness is preserved for the MgO[100] surface, in agreement with experiment which shows virtually no relaxation or rumpling [28]. The in-plane [$\sqrt{2}a \times (3/\sqrt{2})a$] dimensions were chosen to accommodate a water layer of $c[3 \times 2]$ symmetry. The height of the simulation cell was 15 Å, corresponding to a 11 Å vacuum (or 8 Å vacuum with adsorbed water). The water adsorption was studied in the coverage range up to 1 ML, by varying the number of water molecules in the simulation cell from 1 to 6.

The adsorption of isolated water molecules was studied in three different configurations. The results for molecular, dissociative (bound to neighboring sites) and dissociative (bound to distant sites) adsorption are summarized in Table I. The dissociation on neighboring surface sites, although stabilized by hydrogen bonding, was less favorable than molecular adsorption. In the most stable configuration, the water molecule adsorbs with one hydrogen bond to a surface oxygen. When the water dissociated at distant sites, the hydroxyl group from water was symmetrically bonded to two magnesium ions. I did not look in detail into the adsorption of isolated water molecules, since it is well established in previous calculations [9,10] that the adsorption is molecular. The binding energies, E_{bind} , are calculated with respect to the water molecule in vacuum and the clean slab. The calculated binding energy is within the range of binding energies

TABLE I. Comparison of molecular and dissociative (at neighboring and distance sites) adsorption of water on MgO[100]. The atoms are named to enable a comprehensive analysis: H_d is donated to the surface. O_a and H_a are the remaining atoms of the water molecule. (See Fig. 1.)

	Molecular	Dissociative (close)	Dissociative (distant)
E_{bind} (kJ/mol)	-36	-26	+48
$R_{O_a-H_a}$ (Å)	0.97	0.97	0.97
R_{H_d-O} (Å)	1.82	1.08	0.97
$R_{O_a-H_d}$ (Å)	1.01	1.44	...
R_{O_a-Mg} (Å)	2.21	1.98	2.07

reported in previous theoretical studies [5,10,11,16]. After confirming that isolated molecules indeed are molecularly adsorbed, a pair of hydrogen bonded water molecules on MgO[100] was studied. The mixed molecular and dissociative adsorption seen in Fig. 1 had a binding energy of -53 kJ/mol, which was lower than for purely molecular adsorption (-38 kJ/mol). In purely molecular adsorption, the gain in energy from the hydrogen bonding is almost perfectly balanced by the raise in energy due to the nonoptimal water-surface interaction. The dissociative pathway, on the other hand, gives a large gain in energy for water aggregation. Since the dissociation is stabilized by hydrogen bond *donation* from the second water molecule, only one of the water molecules dissociates and the other adsorbs molecularly. The remaining hydroxyl group also accepts a hydrogen bond from the surface hydroxyl group formed from H^+ . A Mulliken analysis is performed by projecting the plane-wave Kohn-Sham orbitals onto the local atomic pseudo-wave-functions. The hydrogen bond donor withdraws 0.07 electrons from the dissociated water molecule. This weakens the interaction of O_a both with H_d and the surface. The elongated O_a-H_d bond is weakened as a result of the hydration and that of the surface hydroxyl $O-H_d$ strengthens. This lowers the barrier for dissociation and the energy of the dissociated form of the water molecule. The existence of a hydrogen bond-donating and -accepting hydroxyl pair on the smooth MgO[100] surface has been proposed in ir studies [7], and also forms the basis of the theoretically proposed structure of the $c[3 \times 2]$ monolayer [16]. The water interaction has a similar effect as the presence of steps on the MgO[100] surface [10]. The hydration forces withdraw on average 0.2 electrons from the MgO[100] which influences the dissociation barrier, through fluctuations in the hydration sphere, and the relative stability of the reactant and product. The presence of mixed molecular/dissociative adsorption on the $TiO_2[110]$ surface has been predicted from density functional calculations [29]. On $TiO_2[110]$ the effect of water interaction is the reverse; isolated water molecules adsorb dissociatively, but at monolayer coverage half of the waters adsorb molecularly.

A 1/2 ML coverage at the MgO[100] surface, corresponding to three H_2O molecules in the simulation cell,

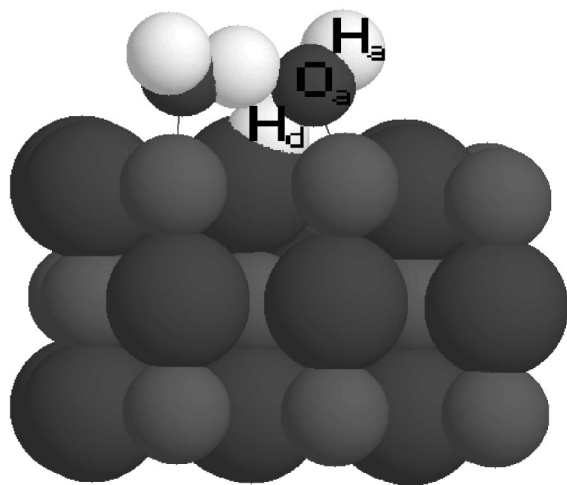


FIG. 1. A mixture of dissociated and molecular adsorption is more stable than purely molecular adsorption, due to enhanced hydrogen bond interaction, despite the fact that the hydrogen bonds from the surface and from the water molecule are at a close angle.

was MD simulated for 1.2 ps at ~ 200 K without any dissociation occurring. Thus, although the mixture of dissociative and molecular adsorption is energetically favored already when only two molecules interact, the barrier for dissociation is too high to occur spontaneously in the short simulation. The water molecules were parallel to the surface and formed hydrogen bonds to each other and to the surface. Then a fourth water molecule was inserted 3.5 \AA over the surface, which approached the surface and within 0.7 ps of MD simulation at ~ 160 K a water molecule spontaneously dissociated. The attraction to the surface and the water interaction lowered the barrier for dissociation. Also, a 3 ps MD simulation at 180 K and a $2/3$ ML coverage on the MgO[100] slab was performed, in which a permanent dissociation occurred within 0.6 ps. I carefully checked the configuration leading to the dissociation and performed several additional shorter MD simulations, in which the temperature of the water molecules was artificially low and/or the lattice parameter was varied. However, the results remained. The water interaction induced the dissociation of water on the defect-free MgO[100] surface. Furthermore, if the water molecule, which stabilized the dissociation by hydrogen bond donation, was deleted, the hydroxyl group and the proton reacted to form water. The barrier for the “backreaction” depends on the momentary geometry, but it can be zero or very small. Thus, the dissociation and reassociation can be very rapid, which makes the dissociation mechanism compatible with the temperature desorption experiments [8]. At $2/3$ ML coverage on the MgO[100], configurations with a higher percentage of dissociated molecules were either higher in energy or unstable, and rearranged to form molecular water in the ratio 3:1 over dissociation.

With the importance of hydrogen bond donation and dissociation in mind, water structures in the ordered

$c[3 \times 2]$ phase were constructed for both $2/3$ and 1 ML coverage, in which two of the H_2O molecules in the simulation cell were dissociated. In geometry optimizations, the system reconstructed itself, keeping the number of dissociatively adsorbed water and the high symmetry, as shown for the 1 ML coverage in Fig. 2. For each coverage, a 1 ps long MD simulation at ~ 200 K was performed to test the stability of the optimized structures. The protons were fluctuating wildly back and forth between waters and hydroxyl groups. At $2/3$ ML coverage, one of the dissociated water molecules reformed, whereas at 1 ML coverage the ratio of molecular and dissociated water molecules was preserved at 2:1. These results, obtained from several short simulations, indicate that at $2/3$ ML coverage dissociation occurs at a ratio larger than 2:1 which is not compatible with a $c[3 \times 2]$ symmetry, in contradiction with previously suggested models [5]. The experimental isosteric heat of adsorption is 85.3 kJ/mol [17]. In comparison, the average binding energy in the ordered $c[3 \times 2]$ phase coverage were -46 kJ , significantly lower than the binding energy for isolated molecules, but higher than that for the pair of water molecules. The energetics during the reactions in the MD simulations was consistent with the energies for the pair water molecules, and it was not possible to derive a trend for the stability of the molecular and dissociated form as a function of coverage. The ratio of molecular and dissociated water molecules is determined by coverage, and at monolayer coverage the ratio is 2:1.

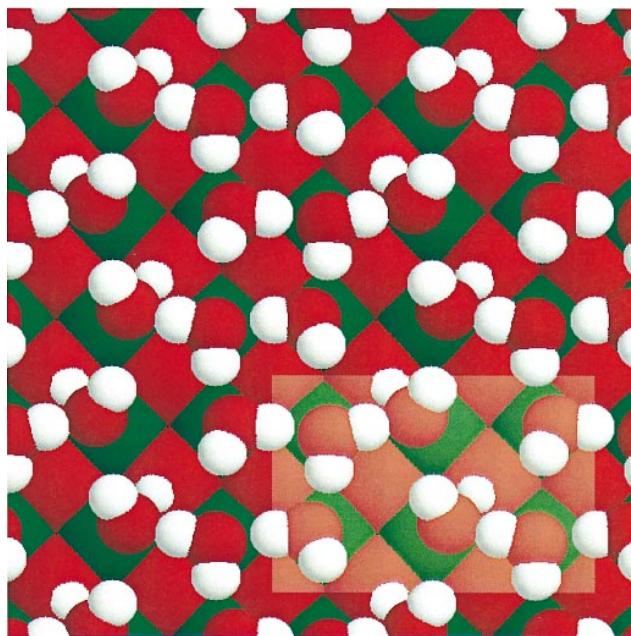


FIG. 2(color). The ordered structure of water on MgO[100] at 1 ML coverage. The highlighted $c[3 \times 2]$ symmetry included the occurrence of a $(0,1/2)$ glide plane in the water overlayer structure, in agreement with experiment [5]. The geometries of the dissociated and hydrogen bond donating water molecules are only slightly different from that in Fig. 1.

From the MD simulation at 1 ML coverage, the vibration spectra of the hydroxyl groups and water molecules, simply extracted from proton velocity auto correlation functions, contained several signals. The $\delta(\text{DOD})$ signal for the water bending mode, $1150 \pm 20 \text{ cm}^{-1}$, confirms the interpretations of experimental data for D_2O on $\text{MgO}[100]$ [5]. The stretching vibrations, $\nu(\text{OD})$, were $2480 \pm 20 \text{ cm}^{-1}$ for the free and weakly hydrogen bonded waters and $2350 \pm 40 \text{ cm}^{-1}$, for the strongly hydrogen bonded waters, but there is also a broad signal in the range $2100\text{--}2300 \text{ cm}^{-1}$ for the bond vibrations, and components from the hydroxyl groups at $1970 \pm 20 \text{ cm}^{-1}$, which is not in agreement with the sharp peaks experimentally observed [5,8].

In conclusion, the presence of a water film significantly alters the chemical activity of the $\text{MgO}[100]$ surface. Above $1/2$ ML coverage the dissociation of water occurs spontaneously within picosecond MD simulations. The dissociation of water is stabilized by hydrogen bond donation. The hydroxyl groups and water molecules were seen to repetitively exchange protons. Thus, the dissociation should give rise to a measurable effect in the proton conduction on the humid $\text{MgO}[100]$ surface. Just as in the aqueous solutions of protons [30], fluctuations in the hydrogen bond network influence the strength of the H-O bonds and trigger the rupture of O-H bonds. These effects are important for surface phenomena, such as catalysis and surface degradation. The mechanism for dissociation will also be of importance for understanding the ordered $c[4 \times 2]$ phase of water on $\text{MgO}[100]$ [5,8,17].

Furthermore, the spontaneous dissociation suggests a mechanism, without reference to defects, for the dissolution of the smooth $\text{MgO}[100]$ surface observed in atomic forces microscopy [4]. The structure in Fig. 2 is consistent with the experimental results, which imply that both hydrogen and oxygen should fulfill the $c[3 \times 2]$ (with a glide plane) symmetry. The previously suggested model for the $c[3 \times 2]$ 1 ML phase [16] is slightly different in structure, but of the same energy and ratio of dissociation. However, the ir spectrum of the $c[3 \times 2]$ phase, which contains three sharp peaks [8], has been interpreted as evidence for a lack of strong hydrogen bonding on the surface. This is not in agreement with the present structure.

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