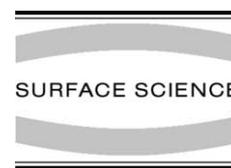




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Structures of adsorbed water layers on MgO: an ab initio study

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Abstract

A systematic search using an ab initio density-functional method has been carried out for energy minima for a monolayer of water on MgO. Minima were sought in which one third of the water molecules were dissociated, and the observed $p(3 \times 2)$ symmetry satisfied. Six such minima were found, three of which are within $300k_B$ per water molecule of the lowest energy structure. We also found a structure with a similar energy with (2×2) symmetry and half the water molecules dissociated. The structures are stabilised by the donation of three hydrogen bonds to each hydroxide ion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Density functional calculations; Chemisorption; Surface structure, morphology, roughness, and topography; Magnesium oxides; Water; Single crystal surfaces

1. Introduction

The structure of adsorbed films of water on a perfect surface of MgO has been a matter of considerable experimental and computational interest for some years. Experimentally, water is found to adsorb reversibly on a flat MgO surface to form a monolayer at temperatures in the region of 200 K. LEED and helium scattering experiments [1–3] indicate a $p(3 \times 2)$ structure with glide planes perpendicular to the long axis of the cell. The reversibility of the experiments was interpreted as

showing that the monolayer was physisorbed rather than dissociatively chemisorbed. This conclusion was generally accepted until ab initio calculations indicated spontaneous formation of a structure with one third of the water molecules dissociated [4,5]. This result has been confirmed by later work [6,7].

Earlier calculations had been performed using classical interaction potentials [10–12] which gave a planar structure for the physisorbed layer with the water oxygens above magnesium ions. The molecules in the monolayer were connected by a two dimensional network of hydrogen bonds and there were no hydrogen bonds to the surface oxide ions. Early ab initio work [9] showed that a single adsorbed water molecule was stable when physically adsorbed was only able to dissociate in the

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presence of defects. However, Odelius [5] studied (also using *ab initio* methods) the consecutive adsorption of water molecules and found that, as the coverage increased, a fraction of the water molecules dissociated. Similarly, Goniakowski and co-workers [4] found that the classical adsorbed monolayer structure spontaneously formed a dissociated chemisorbed layer. Delle Site et al. [6] found minima on the potential energy surface of a monolayer of water in a (3×2) cell corresponding to both physisorbed and dissociated states. The physisorbed structure was not very stable and in a MD run at 300 K spontaneously dissociated to an asymmetric state with no glide plane, but with a lower energy than the structure of Giordano et al. [4]. This discovery of lower energy dissociated states has led us to attempt a systematic search for minima which maintain the observed (3×2) cell with a glide plane. The results of this search are reported in this letter. We have found six such minima, the lowest of which is 0.39 eV per unit cell lower in energy than the original configuration of Giordano et al. [4]. We also investigated (2×2) structures with 50% of the molecules dissociated and found an energy minimum with energy very similar to the lowest (3×2) energy minimum. In all these low energy minima the OH^- ion formed by the dissociation of a water molecule is stabilised by accepting at least three hydrogen bonds.

2. Technical details

The calculations have been performed in the same way as in our previous work [6]. We used the finite-temperature method of Alavi et al. [13] (FEMD). In this method, a free energy functional is optimised, yielding at self-consistency the electronic free energy in the framework of density-functional theory, pseudopotentials and plane-wave basis sets. This method can handle partial occupation of states at the Fermi level. A Troullier–Martins [14] pseudopotential was used to describe the oxygens, a local pseudopotential was used for the hydrogen, and for magnesium the pseudopotential in the form developed by Gonze et al. [15] was used. The plane wave cut off was 60 Rydberg. The BLYP generalised gradient ap-

proximation density functional was used as it seems to give the best results for H-bonded systems [16].

In all the simulations the magnesium oxide surface was modelled by a slab of three layers of (001) crystal planes, the bottom two of which were fixed. The size of the simulation box for the 3×2 surface unit cell simulations was $L_x = 8.94 \text{ \AA}$, $L_y = 5.96 \text{ \AA}$ and $L_z = 17.88 \text{ \AA}$, so that the thickness of the vacuum between the water layer and the bottom layer of the image slab of MgO is equal to about 11 \AA . The calculations were performed at the Γ point. A few calculations were performed on a larger system corresponding to a 6×2 surface unit cell in order to compare the energies of 3×2 and 2×2 structures.

3. Symmetry and possible structures

Fig. 1 shows the sites in the basic (3×2) unit cell. The small circles labelled A, B and C correspond to magnesium ions in the top crystal layer. Oxygen atoms from water molecules or hydroxide ions in the water overlayer sit over these sites. The large circles labelled x, y and z represent oxide ions in the top crystal layer and are possible sites for dissociated protons. Glide planes pass through the sites z (dashed line) and A (vertical lines on the cell boundaries). Sites with the same label are related

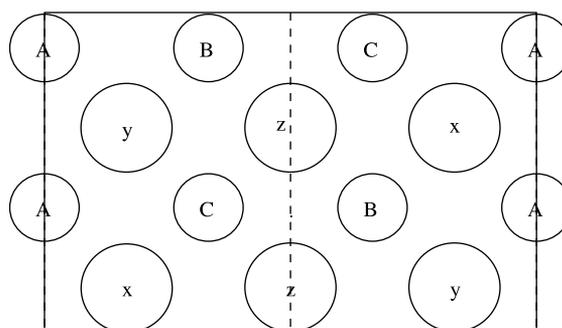


Fig. 1. Top view of a 3×2 surface unit cell of MgO showing magnesium sites as small circles and oxide sites as large circles. Glide planes run vertically through the centre (dashed line) and at the right and left hand cell boundaries. Pairs of sites related by the glide plane symmetry have the same labels. Sites A, B, and C may have hydroxide ions formed by dissociation of water molecules while sites x, y or z contain the dissociated protons.

by these glide planes and must contain the same species with the correct relative orientations. Thus the possible positions of the hydroxide ion in a full monolayer with two out of six water molecules dissociated are on sites A, B or C. Such configurations can be labelled by the positions of the hydroxide ions and the dissociated protons, for example an Ax configuration has hydroxide ions on the A sites and the dissociated protons on the x sites. As Cx, Cy, Cz and Ax configurations are equivalent to By, Bx, Bz and Ay configurations respectively by translation of half a cell along the glide plane, there are five independent types of configuration, Ay, Az, Bx, By, Bz. It was found that for each of these there are two possible relative orientations of undissociated water molecules on inequivalent sites which are consistent with a hydrogen bonding network. We distinguish these by the numbers 1 and 2 in the configuration labels.

We prepared input configurations corresponding to these ten distinct possibilities and performed energy minimisations on each using the BFGS method [17]. Although the glide plane symmetry was not constrained during the energy minimisation, the deviations from this symmetry in the final structures was very small.

4. Results

From the 10 starting configurations six minima were found. The energies of these minima are given in Table 1. The four starting configurations

Table 1
Relative energies of potential energy minima

Symmetry	Energy per unit cell/eV ^a	Energy per water/K	Reference
Bz2	0.0	0	
Bz1	0.06	110	[6]
Bx1	0.16	300	
Bx2	0.27	530	
By2	0.31	590	
By1	0.44	860	
2 × 2		200	
GGs (BZ)	0.39	760	[4]
Asymmetric	0.20	380	[6]

^a See text for discussion of accuracy.

with hydroxide ions on the A sites changed to one or other of these minima by where they would be adjacent to each other. This change occurred by movement of a proton from a water molecule to a hydroxide ion along a hydrogen bond in a process akin to the Grotthus mechanism for the conductivity of protons. The instability of configurations with hydroxide ions on A sites is probably because the Coulomb energy of the necessarily adjacent ions is unfavourable and it is more difficult to find the three adjacent hydrogen bond donors for each hydroxide ion which are necessary for its stabilisation.

We found two general principles to apply in all the energy minimisations. These were, first, that the dissociated protons did not move or recombine, although bound protons could move along hydrogen bonds within the ad-layer of water changing the positions of the hydroxide ion, and secondly, that in all the final energy minima the hydroxide ions were stabilised by accepting at least three hydrogen bonds. Fig. 2 shows two of the minima with the experimental symmetry (Bz2 and Bx1). The first of these is the most stable configuration that we found. In these figures four 3×2 unit cells are shown. Undissociated water molecules are shown in grey, while dissociated water molecules are in dark grey. Glide planes through the z sites (see Fig. 1) run vertically through the centre and the edges of these figures while glide planes running through A sites run vertically through planes one quarter and three quarters across the figures. In both configurations sites on the the A type glide planes are occupied by columns of undissociated (grey) water molecules. The main difference between these two configurations is in the positions of the dissociated protons. In the Bz2 configuration these lie in z positions along the glide planes while in the Bx1 configuration they lie in a zig-zag arrangement. In these figures hydrogen bonds are drawn between hydrogen atoms and oxygen atoms which are less than 2.2 Å apart. In both configurations, and indeed in all the minima we found, the hydroxide ion is stabilised by the donation of three hydrogen bonds to its oxygen atom. However, the origin of these hydrogen bonds differs in different configurations; in the Bz2 configuration two undissociated water molecules

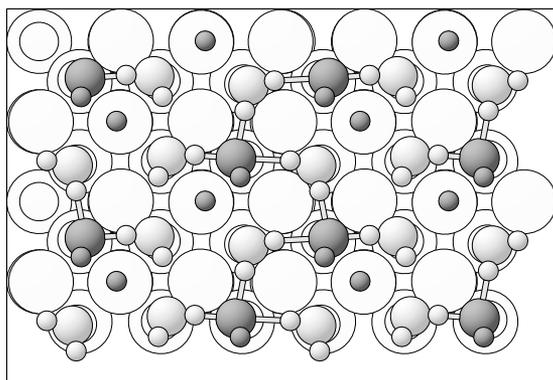
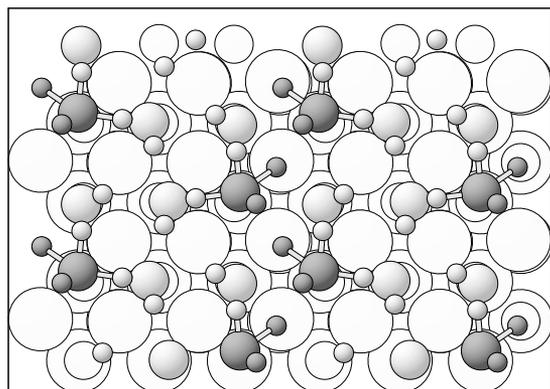


Fig. 2. Above: view of the (3×2) configuration with the lowest energy (Bz2). Below: Another low energy configurations (Bx1). Undissociated water molecules are shown in grey and dissociated ones in dark grey. Hydrogen bonds are shown. Each view is of four unit cells with glide planes running vertically down the centre, the edges and half way between these points.

and the dissociated hydrogen donate hydrogen bonds, while in the Bx1 configuration three undissociated water molecules are involved. These sorts of differences occur in the other configurations which are not shown here.

Table 1 also shows the energies of the structure of Giordano et al. [4] (labelled GGS and with symmetry of type Bz1) and the asymmetric structure found in our earlier work (labelled asym). We note that both these structures are significantly higher in energy than the three lowest energy structures found in our systematic search.

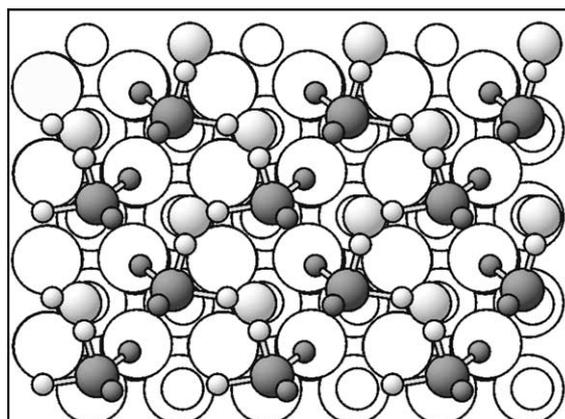


Fig. 3. View of the (2×2) configuration. The view shows six unit cells and contains the same number of sites as the views in Fig. 2. Undissociated water molecules are shown in grey and dissociated ones in dark grey.

Examining the Bz2 structure shown in Fig. 2 suggested that a 2×2 structure with very similar hydrogen bonding could be made by removing the column of undissociated water molecules (grey) on A sites. We prepared a structure of this type and performed an energy minimisation. In order to get a fair comparison between the 3×2 and 2×2 structures, it is necessary to use the same conditions for the calculations. To do this, we prepared 6×2 unit cells by doubling the Bz2 configuration and tripling the 2×2 configuration and performed further energy minimisations on these bigger unit cells. The energy of the 2×2 structure which is shown in Fig. 3 is similar to that of the other minima. The structure still has glide planes.

5. Discussion and conclusions

The main conclusion of this work is that there are several low lying minima on the potential energy surface of an adsorbed monolayer of water on the (001) surface of magnesium oxide which are consistent with the experimental observations and which have one third of the water molecules dissociated. An additional, and surprising, result is that there is a low lying minimum on the potential

energy surface with half of the water molecules dissociated.

One may ask whether there are many more minima on the surface. We believe that the set of minima found here represents all the low lying minima which are consistent with the experimental symmetry. We have assumed that the water and hydroxide ion oxygen atoms lie over magnesium ions and that dissociated protons are bonded to oxide ions in the top crystal layer. We have shown that this gives five different symmetry types in which the positions of the hydroxide ions and dissociated protons are specified with relation to the magnesium ions and oxide ion positions in the top layer. Low lying minima must be of one of these symmetry types. These minima must also have extensive hydrogen bonding within the water layer. Each starting configuration was set up with the water molecules aligned to form a hydrogen bonding network and it was found that, for each symmetry, there were only two possible relative orientations of the two types of undissociated water molecules which gave a good network. These were used as starting points for the minimisation.

It is obviously important to consider the possible causes of error in the relative energies and to estimate their importance. The main sources of error are the density functional, finite size effects and errors in the minimisation procedure. We estimate that the error introduced by the density functional may be as much as 0.1 eV per unit cell or 200 K per water molecule. This is the largest source of error, and it is well known that the available density functionals do not describe hydrogen bonded systems very accurately. The next largest source of error is the use of a small system size. Although the absolute errors in the energy in these calculations is probably quite large, we found that adding k points did not change the forces significantly and we believe that the relative energies of different configurations due to finite size effects are significantly less than the error introduced by the functional. Finally the errors due to the minimisation process are less than 0.015 eV per unit cell.

In Table 1 four minima (including the 2×2 structure) have energies within 300 K per water

molecule of the lowest minimum. These are all likely to be thermally accessible and their relative energies are similar to the errors in the calculation. In a recent paper, Giordano et al. [8] point out that, even within the well of one potential energy minimum, finite temperature effects may affect the comparison with experimental data. The possibility of several accessible minima would further affect this comparison. There has been some recent neutron scattering work on this system [18]. The existence of the $p(3 \times 2)$ phase was confirmed, but it was found that the coherence length was only about 35 Å. The 2×2 structure found in this work would interface well with the Bz1 or Bz2 structures, giving a very low energy defect. This could help to explain the short coherence length. It is also possible that local regions of different minima reduce the coherence length.

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