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Adsorption of water on MgO(100): A singular behavior

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Interaction-potential minimization and molecular-dynamics simulations show that a perfect MgO(100) surface accomodates very stable flat water monolayers differing only by the mutual orientations of the molecules above the cations, without evidence for significant hydrogen bonding with the substrate and between the H_2O molecules. Increasing coverage leads to the occurrence of an upper solid versus liquidlike structure not hydrogen bonded to the stable monolayer, which tends to tear up at 300 K. These results are in good agreement with recent experimental data. [S0163-1829(98)03620-0]

The fascinating field of water adsorption on various substrates, of fundamental interest for scientists,[1] has gained in addition a revival of activity this past decade with the development of surface technology to determine the conditions that favor physisorption vs chemisorption of molecular water or dissociation.[2] The role of defects in initiating the dissociation of water has been shown to proceed[3,4] via a complicated pathway implying, for instance, on MgO, energy balance in the hydroxyl formation. Aside from dissociation, water is generally known to adsorb molecularly on clean metals or dielectrics, at least below 300 K. For instance, recent scanning tunneling microscopy studies[5] have demonstrated the development of ordered two-dimensional (2D) ice layers of water on Pt(111) and stable bilayer phases around 130 K were deduced[6] from helium atom scattering (HAS) experiments. The scenario generally admitted, proposed on the basis of molecular-dynamics simulations,[7] is that water forms icelike hexagonal structures with the oxygens bound to Pt atoms while the second layer is hydrogen bonded to the first layer and, beyond, transition to the bulk behavior occurs. Similar conclusions were drawn for other metals[8–11] with, however, some differences depending on the substrate geometry and electronic properties, and still more complex results were obtained on semiconductors regarding the fact that water dissociates or molecularly adsorbs.[12–15]

Water adsorption on ionic/partially ionic crystals is characterized by the presence of strong electrostatic surface fields and field gradients which can compete with the lateral binding between H_2O molecules and could create a favorable situation for the formation of stable 2D layers. Helium scattering experiments on UHV cleaved $CaF_2(111)$ surface showed the occurrence of a $p(4\times4)$ phase that was interpreted in terms of the formation of water hexamers.[16,17] On NaCl(100), infrared spectroscopy and low-energy electron diffraction (LEED) data[18,19] concluded to the presence of an ordered quasihexagonal $c(4\times2)$ bilayer structure and helium scattering data[20] led to the formation of a (1×1) condensed phase for which nearest-neighbor water molecules are relatively far apart (3.96 Å) in the range 80–160 K. Periodic Hartree-Fock[21] and semiempirical calculations[22,23] showed that the (1×1) monolayer and the (4×2) bilayer phases have a similar binding energy per molecule, and that the latter should be stable at a larger water density than the monolayer as a result of the increasing influence of the lateral interactions.

The aim of this paper is to show that the clean (100) surface of MgO behaves as a singular substrate for water adsorption since the distance a ($a=2.98$ Å) between oxygen (magnesium) sites is close to the oxygen-oxygen distance d_O between hydrogen bonded molecules ($2.67\leqslant d_O\leqslant 2.90$ Å). This small mismatch should favor the formation of stable ordered 2D layers, in contrast to the previous situations. Recent experiments including (LEED),[24] HAS,[25] and IR spectroscopy[26] agree that water forms a very stable $p(3\times2)$ phase with molecular density around 6–8 per unit cell and a denser phase containing 12–16 molecules which disappears at $T>180$ K due to partial water desorption. The spectroscopic signature of these two phases is very different since the dense phase gives broad IR lines whereas the IR bands of the other phase are quite narrow and less shifted. Molecular-dynamics (MD) and Monte Carlo (MC) simulations[27] revealed at 300 K a densely packed first layer with water molecules aligned $-17°$ and $+30°$ with respect to the surface plane while the other layers appear more diffuse and become more liquidlike.

Two species of complementary calculations have been performed here to study the structure of water on MgO(100). First, an energy minimization procedure (EM) based on a numerical conjugate-gradient approach at 0 K is applied to commensurate $(m\times n)$ phases (m and n integers) of a monolayer containing one molecule per Mg site after it was demonstrated that larger and smaller coverages are energetically much less favorable. Then finite-temperature calculations are conducted using MD simulations for an increasing number of molecules inside a square $12a\times12a$ simulation patch, i.e., from 144 molecules for the monolayer up to 400 molecules for the multilayering. The substrate and the molecules are assumed to be rigid.

The interaction potential between the water molecules is represented by the TIPS2 potential,[28] which has proven to be very efficient in describing the behavior of liquid water and ice. The interaction between water and the substrate is the sum of electrostatic and semiempirical dispersion-repulsion contributions,[29] which appear to give a good compromise between accuracy and tractability in MD. The equilibrium configuration of a single H_2O admolecule is above the cation

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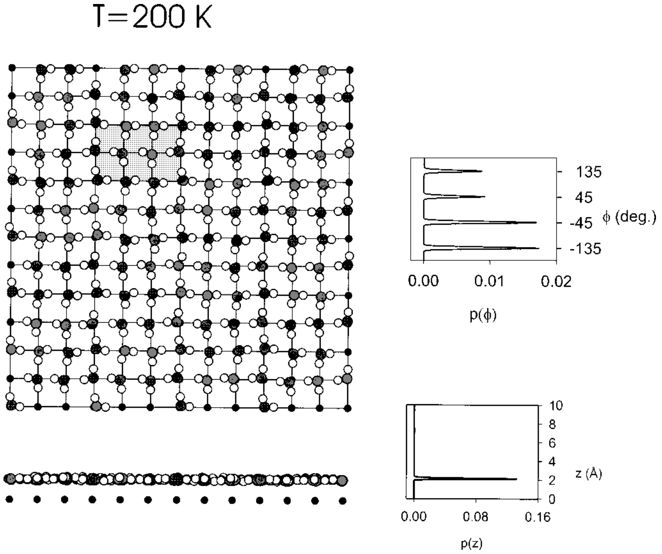

FIG. 1. Front view and bottom view of the (3×2) monolayer structure at 200 K. The large square represents the simulation patch while the small squares define the unit cell of MgO(100). Black circles are Mg atoms of this substrate, gray circles and empty circles correspond to oxygen and hydrogen atoms, respectively. Upper right: distribution $p(\phi)$ of the orientation ϕ of the water molecular symmetry axis in the plane parallel to the surface. Bottom right: distribution function $p(z)$ of the molecule-surface distance z.

site with the molecular plane parallel to the surface and the hydrogen pointing nearly toward the adjacent Mg ions, i.e., leading to four equivalent orientations for the H atoms. This configuration is consistent with periodic Hartree-Fock results[30] while in the Car-Parinello approach[3] one hydrogen forms a bond with an oxygen of the surface and the other H stands upright. Both approaches concluded that water binds to the surface without appreciable charge transfer.

The EM procedure applied to the complete water monolayer (each Mg site occupied in average) shows that several low commensurate phases $(m\times n)$ have an adsorption energy per molecule ranging between -940 meV and -910 meV. The experimental value of the isosteric heat of adsorption is 885±22 meV at $T=200$ K.[24] The (1×1) phase with one molecule per Mg site having the same configuration and the same holding energy as the single admolecule is the most stable at 0 K. The lateral energy represents about 40% of the total potential, i.e., 385 meV (experimental value 365±100 meV). All attempts for finding more stable configurations with successive integer values of m $(=1,\ldots,4)$ and n $(=1,\ldots,4)$ failed since increasing the size of the unit cell led to slightly less stable structures differing by the mutual orientations of adjacent H_2O molecules in a plane parallel to the surface (Fig. 1). Calculations performed with more elaborated potential forms (higher electrostatic contributions or polarizable water approach) led to the same conclusions.[29]

The MD calculations have been performed first for one complete monolayer at various temperatures (150, 200, and 300 K). At any of these temperatures (less than 300 K) we start the simulation from an initial $(m\times n)$ structure $(m=1,2,3$ and $n=1,2)$. The structure obtained in the thermal equilibrium regime remains the initial structure due to the strong barrier that prevents the mutual reorganization of the molecular orientations. Nevertheless, MD results indicate that the (3×2) phase appears to be the most stable above 200 K with an energy per molecule equal to -851 meV, instead of the (1×1) geometry found in the EM procedure at 0 K (Fig. 1). Then, keeping the same $12a\times 12a$ patch, we increase the number of water molecules in the simulation box by considering two hexagonal bilayers containing 256 molecules and having the ice structure[31] as the starting configuration. Results at 150 K as at 300 K lead to the formation of a neat monolayer in which 12×12=144 water molecules

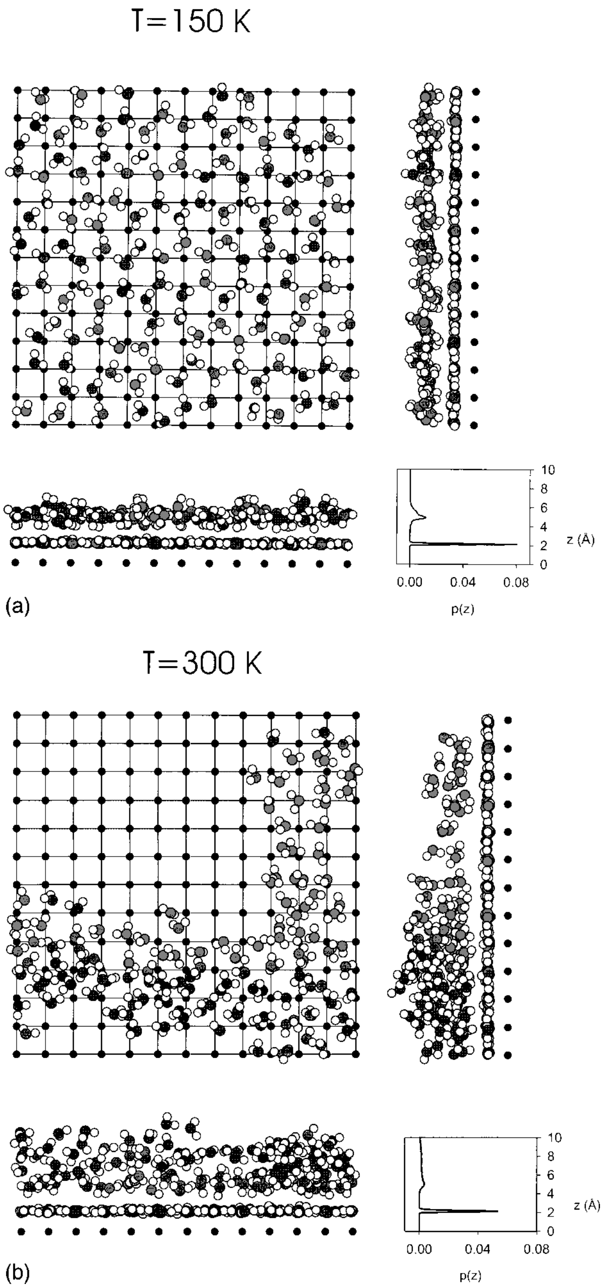

FIG. 2. Monolayer plus upper structures at 150 K (a) and 300 K (b). Top view: only the geometry of the upper structure is represented, since the geometry of the monolayer is similar to that shown in Fig. 1. The side views (bottom and right views) include the geometry of the monolayer and upper structure water molecules. Bottom right: distribution function $p(z)$ of the molecule-surface distance. Note the flat structure of the monolayer for the two temperatures.

participate in a mixing of (1×1), (2×1), and (3×2) phases, while the 112 remaining molecules that do not participate to the formation of the monolayer are more or less ordered above the first layer. This feature shows that the adsorption on MgO is able to destroy the initial ice structure and to form a very stable flat monolayer, as shown by the very narrow distribution of the layer-substrate distance [Fig. 2(a)] and the distribution peaks for the water orientation in the plane parallel to the surface.

In order to test the stability of the adsorbate, we form at $T=150$ K the stable (3×2) monolayer structure and deposit on it a bilayer having the hexagonal ice structure in the simulation box. No change is observed for the stable monolayer and only small distortions of the bilayer can be detected in various snapshots (not presented here). Increasing T up to 300 K shows that the monolayer remains very stable whereas the bilayer tends to tear up and to evolve toward a 3D structure [Fig. 2(b)]. Adding more water molecules does not change the results, indicating that the monolayer clearly forms an entity with the substrate although it is not hydrogen bonded to MgO, while the other molecules that do not belong to the monolayer tend to arrange themselves in a solid vs liquidlike structure. The distribution function [Figs. 2(a) and 2(b)] of the molecule-surface distances for this monolayer + bilayer system clearly shows the stability of the first layer and the broadening characteristic of the formation of a 3D-like structure. Note that this 3D-like structure is not hydrogen bonded to the first layer as shown in the side view [Fig. 2(b)].

The diffusion coefficient D of the water molecules calculated in the monolayer and 3D phase characterizes the mobility of the molecules in these layers. For the monolayer, the value of D along the two directions x and y does not change significantly when T rises from 200 to 300 K ($D=4\times10^{-6}$ cm^2 s^{-1}) while the value of D for the upper structure increases from 4.5×10^{-6} cm^2 s^{-1} at 150 K to 9.0×10^{-5} cm^2 s^{-1} at 300 K. Note for comparison the value of D for liquid water at 300 K equal to 3×10^{-5} cm^2 s^{-1} (Ref. 32) which indicates that the monolayer is ''frozen'' by the substrate whatever the temperature and that the upper structure at 300 K has a behavior intermediate between liquid and solid water due to its interaction mainly with the monolayer.

Last, we calculate the strength of the hydrogen bond between water molecules in the monolayer and in the upper layers by determining the distribution d_H of the distance $\mathrm{H}_i \ldots \mathrm{O}_j$ in the bond $\mathrm{O}_i\text{-}\mathrm{H}_i \ldots \mathrm{O}_j$ connected to two adjacent molecules i and j and of the angle $(\mathbf{O}_i\mathbf{H}_i,\ \mathbf{H}_j\mathbf{O}_j)$. We obtain a peak in the distribution d_H centered around 2.0 Å for the monolayer while the peak maximum for the upper layers occurs at 1.86 Å at 150 K and 1.89 Å at 300 K. The first value is consistent with the commensurate structure for which the Mg sites at a mutual distance of 2.98 Å are occupied by the water oxygens and the $\mathrm{H}_i \ldots \mathrm{O}_j$ distance is equal to $2.98-0.96$ Å$=2.02$ Å, yielding no clear hydrogen bonding; the second value corresponds rather to the solid vs liquidlike structure yielding significant hydrogen bonds. From the examination of the correlation diagram between the O-H stretching frequency shift and bandwidth and the corresponding d_O distance[1,3] we expect no significant shift and broadening of the peak associated to the water stretching mode in the (3×2) monolayer since the mean value of d_O is 2.98 Å. By contrast, for the upper structure, the decrease of d_O ($d_\mathrm{O}\sim2.76$ Å) gives a redshift of about 200 cm^{-1} and a broadening that can reach 100 cm^{-1} for the upper structures. This result is in close qualitive agreement with the IR data,[26] which display a small shift (~50 cm^{-1}) and a narrow profile ($\sim5-10$ cm^{-1}) of the signals connected to the monolayer and a much larger line shift (~250 cm^{-1}) and broadening (~200 cm^{-1}) for the dense phase.

To conclude, we have shown that water forms a well-ordered and very stable (3×2) first layer on the clean MgO(100) surface. The layer/substrate and intralayer interactions are mainly electrostatic, without evidence of hydrogen bonding, implying charge transfer. Although the energy per molecule is typically around 0.9 eV, it is a physisorption process. Above this layer, water has a structure that looks like the 3D solid or liquid phases depending on temperature. This upper structure displays hydrogen bonds but it is not H bonded to the first layer and it appears much more sensitive to a temperature increase. This behavior can be interpreted as a coating of the MgO surface by a first water layer, above which additional water molecules tend to self-arrange in a hexagonal structure. As far as we know, it is the first substrate that, from a physisorption process, can display such a stable monolayer in very good registry with the surface before hexagonal structures grow at higher H_2O coverage. Indeed, for most of the other substrates, the adsorption clearly proceeds directly from a quasi-ice-like geometry. Further analyses are nevertheless required to understand how these results could be modified by the presence of surface defects, consideration of substrate dynamics, the flexibility of the water molecules, and the potential accuracy.

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