

Hydrolysis at Stepped MgO Surfaces

Walter Langel* and Michele Parrinello†

IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

(Received 25 February 1994)

We study the adsorption of water on MgO surfaces with the Car-Parrinello method. Our simulation shows that an H₂O molecule in the proximity of a perfect (001) surface is physisorbed. The binding energy is rather small and the molecule desorbs at modest temperatures. We also simulated a stepped surface. On this surface the dissociation of water proceeds very rapidly. Our simulation is the first of this kind and agrees with experimental evidence.

PACS numbers: 81.60.Dg, 31.20.Sy, 33.10.Gx, 82.65.My

Magnesium oxide is a widely used high-temperature ceramic material. It crystallizes in well-defined cubes of rock salt structure. The most stable crystallographic surface of crystalline MgO is the (100) plane. Planes with Miller indices higher than (100) facet into steps of (100) surfaces [1]. Unless maintained in an ultrahigh vacuum (UHV) environment, MgO readily adsorbs water. The understanding of its surface properties is essential for applications as a support for metal catalysts and high-temperature superconductors. However, in simulations of processes such as the deposition of metal clusters on the MgO surface, the coverage by water or hydroxyl groups is not taken into account [2]. Furthermore, it is well known that the surface hydroxyl groups may influence other properties of this oxide, such as its mechanical response.

The mechanism of the water adsorption on MgO has been studied intensively both experimentally and theoretically. Infrared absorption studies have observed the disappearance of the H₂O bending mode from which it has been deduced that H₂O chemisorbs. There is a controversy in the literature about the chemical activity of the (100) crystallographic surface. Microgravimetry indicated that MgO exposed to air is completely covered by chemisorbed water, including the (100) surfaces [3]. In contrast, an ultraviolet photoelectron study conducted under UHV conditions [1] shows that the coverage of (100) is significantly lower than that of the (111) surface. The authors of [1] argue further that the good coverage of the (111) surface is due to the large number of steps in the microfaceted surface. In addition the water chemisorbed on the (100) surface is attributed to the presence of cleavage defects [(1-5) × 10⁵ steps/cm [4]] on this surface. MgO exposed to air and then baked showed irreversible damages owing to an increased number of defects.

Attempts were made to determine by static calculations whether H₂O could be chemisorbed on the perfect (001) surface [5,6]. The general consensus was that this is energetically unfavorable. The only attempt to calculate a defective surface structure to our knowledge is that of Catlow *et al.* who, at the Hartree-Fock level, use a very simplified and rather unrealistic geometry [7].

More realistic geometries have been considered only at the semiempirical level.

Here we study this problem using the approach of Car and Parrinello. Its main advantage over the more conventional studies described above is that it allows the system to evolve spontaneously following the trajectories dictated by accurate *ab initio* interatomic forces at finite temperature. This permits the atoms to move along complicated pathways. Recently, Car-Parrinello-like methods have been applied successfully to the study of bulk MgO and its defects [8] as well as bulk water [9]. In the present Letter, we evaluate the properties of MgO surfaces and simulate the hydrolysis process both for perfect and defective surfaces. We find that the defects, in particular the steps, play a crucial role in the hydrolysis process.

The Car-Parrinello method has been reviewed in [10]. In order to describe O efficiently we use a variant of the method employing the supersoft pseudopotentials of Vanderbilt [11] for O and H as developed in a recent simulation of water [9]. The pseudopotential for Mg was of the usual norm-conserving type [12]. For an accurate description of the H bond it was found essential to supplement the local density approximation with the generalized gradient correction. We shall use the gradient corrections for the exchange part of the pseudopotential as given by Becke [13]. We have verified the accuracy of our approach by making a series of calculations of the MgO molecule and of bulk MgO (Table I). The bulk calculations were done with cells of 8 and 64 atoms, respectively, using the $k = 0$ point in the Brillouin zone of the electronic wave functions. The results showed no significant change, indicating that the use of $k = 0$ sampling over the Brillouin zone is justified for this ionic compound.

After assuming an initial structure of nuclear configurations, we optimized the corresponding electronic charge densities starting from arbitrary wave functions by a steepest descent method. The optimized atomic structures were then determined by simulated annealing. Typically this meant heating the system for 5000 time steps from 5 to 50 K. After annealing, which initiated significant thermal fluctuation of all atomic coordinates, a further run of 3-5000 steps was started without temperature

TABLE I. Theoretical and experimental results for the MgO molecule and bulk MgO.

	Equilibrium distance of the molecule Å	Vibr. freq. $n = 0 \rightarrow 1$ of the molecule cm^{-1}	Lattice constant of the bulk Å	Bulk modulus Mbar
Theory	1.75	775	4.27	1.59
Experiment	1.75 [16]	756 [16]	4.21 [17]	1.55 [18]

control. The time step in all runs was 7 a.u. or 0.169 fs; the μ parameter of the Car-Parrinello Lagrangian was 1100 a.u. This choice yielded a very satisfactory energy conservation and adiabatic decoupling of electronic and ionic degrees of freedom.

The simplest MgO surface is the (001) plane. We simulate such a plane with an infinite slab oriented perpendicular to the z direction consisting of three (001) planes of four Mg and four O atoms each. It was placed at the bottom of a cell with the dimensions $\sqrt{2} \times \sqrt{2} \times 4$ MgO lattice constants or $5.94 \times 5.94 \times 16.9 \text{ \AA}^3$. Periodic boundary conditions were applied in all three directions. The large period along z allows decoupling between the slabs. In the x - y plane the cell axes were in the (110) and $(\bar{1}10)$ directions. On top of the third layer the adsorbed water molecule, OH group, or H atom could be positioned. This very thin slab gives the central layer a charge distribution similar to that of the bulk [5]. We keep the bottom layer fixed at the equilibrium lattice constant in order to mimic an extended substrate. The top layer showed a very small inward contraction of less than 2% of the bulk Mg-O distance, but it exhibited no appreciable corrugation. This latter feature is in agreement with the results of He atom scattering from (001) planes of MgO single crystals [14,15].

We then performed a series of calculations to determine whether and how a water molecule can be adsorbed on the perfect (001) surface. Two initial configurations were used. In the first one the water O atom was positioned as an adatom vertically on top of a Mg atom of the surface in a distance equal to the Mg-O distance in the lattice. One of the two H atoms was placed in between this O adatom and an O atom of the surface. The other one faced away from the surface. The initial distances between the O adatom and the two H atoms as well as the angle H-O adatom-H were the same as in the free water molecule. In this starting configuration the angle θ between the Mg-O adatom axis and the O adatom-H bond is 135° , corresponding to a Mg-O-H angle of 45° . This configuration was chosen so as to optimize the probability of proton transfer to the surface. Two calculations were done, one at about 40 K with relaxation of the upper plane of MgO and the water molecule, and one at about 200 K with relaxation of the two upper planes. At low temperatures the water molecule was physisorbed in a stable configuration. One H atom was hydrogen-bonded to the surface; the other one was free. In this run the bending mode ν_{HOH} of water was observed at 1480 cm^{-1} ,

confirming that no chemisorption at all was detected. At higher temperatures a significant relaxation of the top two MgO planes is observed. The Mg and the O atom, to which the adsorbed water molecule is linked, are displaced in the z direction by about 0.9 Å. The H atom assumes a nearly symmetric position between the two O atoms. Eventually the water molecule was desorbed in agreement with experiment [3].

In order to exclude the possibility that a particularly unfavorable initial condition for chemisorption had been chosen, the motion of a water molecule on the surface was simulated starting from a second initial configuration. The O atom of this molecule was placed 3.2 Å above the MgO surface at a position not commensurate to the MgO lattice in order to avoid symmetry effects. The two H atoms faced away from the surface. For the first 0.3 ps of a free molecular dynamics run the molecule rotated such that one H atom faced towards one surface O atom. Owing to attractive forces between the molecule and the surface, the O atom approached a surface Mg atom to a distance of about 2.1 Å, i.e., approximately the MgO equilibrium distance. One of the water H formed a strong hydrogen bond with one of the surface O, without undergoing proton transfer to the surface. The other H atom was not hydrogen bonded. This configuration was stable for about 0.5 ps after starting until the end of the simulation (0.93 ps), and no dissociation by proton transfer to the surface was observed. For the ideal surface the emerging picture is one in which the water molecule is simply physisorbed and can be easily desorbed at moderate temperature, as observed in experiment.

As discussed above, the perfect (001) plane is not a very realistic geometry for comparison with experiment. The UHV cleavage of MgO single crystals for preparing well-defined (001) planes is not a method of direct interest for this application. Usually the material is used with a water layer or baked to remove the chemisorbed water. This introduces numerous defects to the surface [4]. The chemical properties of these defects may differ strongly from those of the perfect (001) plane. The chemisorption of water is often assumed to proceed preferably there [1,4].

In order to simulate this specific chemical activity of defects, a stepped geometry was defined for the MgO substrate. It consisted of two (110) layers with 2×3 atoms each, on which a triangular step is put (Fig. 1), and corresponds to faceting of a (110) plane. Annealing was simulated to check whether this geometry is subject

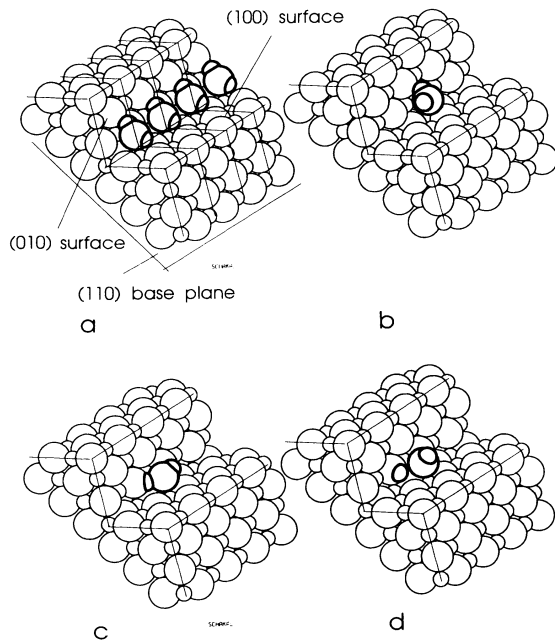


FIG. 1. Step geometry for the facet simulation. Three (011) planes are formed by 2×3 atoms. A roof of six atoms is arranged on top of them. By means of the cyclic boundary condition, steps of (100) planes are formed with a width of two lattice constants or 8.4 \AA , as indicated by the lines. Eight MgO cells are drawn to demonstrate the effect of the cyclic boundary conditions. Only the four water molecules in one step are shown (bold lines). (a) Starting conditions ($t = 0$) of a molecular dynamics run: An undissociated molecule of water is adsorbed inside the step, so the O atom continues the regular MgO lattice. The step and the periodic continuation of the cell of 27 atoms are indicated by lines; eight cells are plotted. The four water molecules in the four cells at the right side are omitted. (b) Like (a), but $t = 0.43$ ps. The water molecule has jumped out of its starting position and reorients. In this and the following pictures all but one water molecule are omitted. (c) $t = 0.55$ ps. The proton transfer between the O atoms in the water and in the surface takes place. (d) $t = 0.96$ ps. The water molecule is dissociated into a H atom on a surface O atom and a hydroxyl group placed on a Mg atom.

to relaxation. The sample was heated up in 0.82 ps from 3 to 150 K and then subjected to a molecular dynamics run without temperature control for another 0.5 ps. For the first 0.4 ps of the heating the distances of the top O and Mg atoms to their Mg and O next neighbors diminished from the ideal value of 2.13 \AA to 1.98 \AA . This geometry was then stable for the following 0.9 ps of the simulation.

Then an undissociated water molecule was placed inside a step [Fig. 1(a)]. Its O atom was placed on a lattice point of the regular O sublattice. The two H atoms faced out of the step, maintaining the geometry of a free water molecule. The sample had been annealed to 25 K for 0.46 ps, and was then subjected to a molecular dynamics run without temperature control. The dissociation occurred between 0.5 and 0.7 ps after the start of the

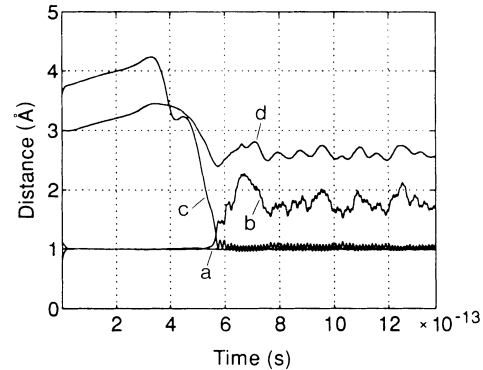


FIG. 2. Interatomic distances in \AA for the dissociation of water in the step as a function of time in 10^{-13} s. Traces a,b: O-H distances in the adsorbed water molecule. c: Distance between the dissociating H atom and the O surface atom adjacent to it after dissociation. d: Distance between the O atom of the water molecule and the surface O atom of c.

simulation and proceeded via a movement of the water molecule out of the original position by about 1 \AA [Fig. 1(b)] to a complicated rotation and consequent reinsertion into the plane [Figs. 1(c) and 1(d)]. Thereby water was decomposed into a hydroxyl group on the Mg atom and a H atom bound to a surface O atom.

In Fig. 2 four characteristic interatomic distances are plotted as a function of time. This allows a quantification of the dissociation process and the determination of the vibrational dynamics of the system. At the start of the simulation both O-H distances (traces a and b) in the free water molecule are close to 1 \AA as expected for chemical bonding. One of these bonds is not affected by the adsorption process (a), whereas the other is stretched to a length of 2 \AA after 0.5 ps (b) and stabilizes at 1.8 \AA after about 0.7 ps simulation time. This increase in bond length clearly indicates that the original bond is broken and replaced by a much weaker hydrogen bond. Trace c shows that the dissociating H atom approaches within 1 \AA to a surface O atom, forming a chemical bond with it. Owing to energy release in the dissociation process, the bond is vibrationally excited. The high frequency of the oscillation in the time interval 0.6–1.4 ps corresponds to the O-H stretching mode. The distance of the water O atom to the nearest surface O is 2.65 \AA after the dissociation process (d), slightly smaller than in bulk MgO (3 \AA). The low frequency oscillations superimposed on this distance correspond to lattice phonons of MgO.

In the stable configuration the Mg-O-H angles were evaluated with respect to the two Mg atoms coordinated to the hydroxyl group of the dissociated water molecule. One of these angles was only 70° , i.e., significantly smaller than in the hydroxyl groups on the (001) plane, whereas the other one was 105° .

The lack of chemisorption on the perfect surface can be rationalized as follows. In the initial configuration [Fig. 3(a)] the O...O distance is large and the orientation of

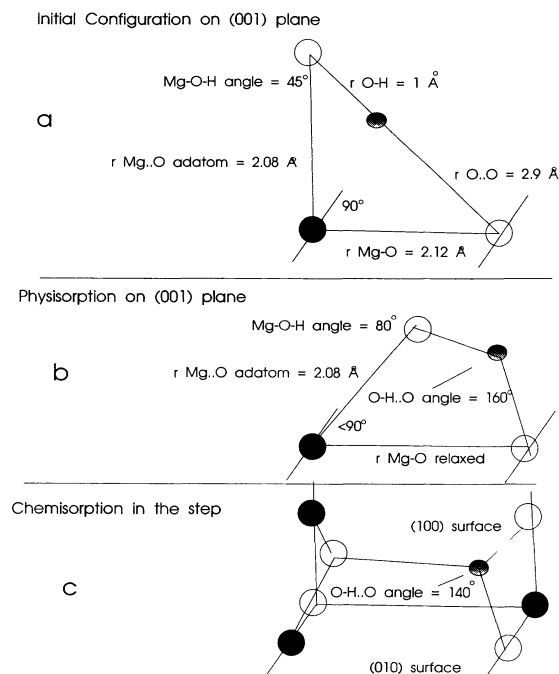


FIG. 3. Schematic drawing illustrating physisorption and chemisorption. Solid circles: Mg atoms; shaded circles: H atoms; and open circles: O atoms. (a) Cut along (010) plane through the initial configuration on the (001) plane. From [19]. (b) Like (a), but after a dynamic run. The O adatom has strongly relaxed thereby reducing the O...O distance across the H atom to 2.6 Å and the O-H...O angle to 160°. (c) Cut through the step geometry parallel to the (100) surface. The O adatom is coordinated to two Mg atoms, the H atom is influenced by a second O atom. The O-H...O angle is 140°, the resulting H bond is weaker than in (b).

the water O-H bond is favorable for proton transfer. This can be seen by the potential energy curve calculated for the proton with all the other atoms fixed. However, as demonstrated in our runs, this is a very unfavorable configuration because the water moves to the final configuration [Fig. 3(b)]. Here the potential for proton transfer is no longer bistable because the two O are so close and the O-H...O angle is of the order of 160°.

In the step geometry, in contrast, the water O interacts with two Mg atoms, and the H atom interacts with two surface O atoms [see Fig. 3(c)]. This prevents the O-H...O angle from getting larger than about 140°. Thus the potential remains bistable and proton transfer can occur. In the final configuration there is an OH⁻ bound to two Mg atoms. The remaining H from the water molecule binds an O of the substrate to form another OH⁻ anion.

In conclusion this calculation demonstrates the role of defects in determining the chemical activity of the MgO surface. To the best of our knowledge this is the first time that this has been achieved with a realistic calculation. We believe this to be an important advancement towards the study of the properties of real-life surfaces as opposed to the study of freshly cleaved surfaces under

UHV conditions.

The Car-Parrinello code has been used in a version rewritten by Kari Laasonen. His support to get the present calculation started is gratefully acknowledged. We would also like to acknowledge fruitful discussions with Franco Buda, Ettore Fois, Jorge Kohanoff, Ursula Röthlisberger, and E. Knözinger. W.L. thanks the Deutsche Forschungsgemeinschaft for a Heisenberg Fellowship and the IBM Research Laboratory, Rüschlikon, for its hospitality during his stay.

* On leave from Universität Siegen, Fachbereich Chemie, D-57068 Siegen, Germany.

† Now at Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany.

- [1] H. Onishi, C. Egawa, T. Aruga, and Y. Iwasawa, *Surf. Sci.* **191**, 479 (1987).
- [2] A. Miyamoto, T. Hattori, and T. Inui, *Appl. Surf. Sci.* **60/61**, 660 (1992).
- [3] S. Coluccia, L. Marchese, S. Lavagnino, and M. Anpo, *Spectrochim. Acta* **43A**, 1573 (1987).
- [4] C. Duriez, C. Chapon, C. R. Henry, and J. M. Rickard, *Surf. Sci.* **230**, 123 (1990).
- [5] C. A. Scamehorn, A. C. Hess, and M. I. McCarthy, *J. Chem. Phys.* **99**, 2786 (1993).
- [6] S. Russo and C. Noguera, *Surf. Sci.* **262**, 245 (1992); **262**, 259 (1992); J. Goniakowski, S. Russo, and C. Noguera, *ibid.* **284**, 315 (1993).
- [7] A. L. Shluger, J. D. Gale, and C. R. A. Catlow, *J. Phys. Chem.* **96**, 10389 (1992).
- [8] A. DeVita, M. J. Gillan, J. S. Lin, M. C. Payne, I. Stich, and L. C. Clarke, *Phys. Rev. B* **46**, 12964 (1992).
- [9] K. Laasonen, M. Sprik, M. Parrinello, and R. Car, *J. Chem. Phys.* **99**, 9080 (1993).
- [10] G. Galli and M. Parrinello, in *Computer Simulations in Materials Science*, NATO ASI Ser. E, Applied Sci., Vol. 205, edited by M. Meyer and V. Pontikis (Kluwer Academic, Dordrecht, 1991) pp. 283-304.
- [11] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990); **43**, 6796 (1991); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, *ibid.* **47**, 10142 (1993).
- [12] R. Stumpf, X. Gonze, and M. Scheffler, Research Report of the Fritz-Haber Institute, 1990.
- [13] A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988); *J. Chem. Phys.* **96**, 2155 (1992).
- [14] P. Cantini and E. Cevasco, *Surf. Sci.* **148**, 37 (1984).
- [15] K. H. Rieder, *Surf. Sci.* **118**, 57 (1982).
- [16] *Spectroscopic Data, Heteronuclear Diatomic Molecules* Vol. 1, edited by S. N. Suchard (IFI Plenum, New York, 1975).
- [17] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963).
- [18] M. J. L. Sangster, G. Peckham, and D. H. Saunderson, *J. Phys. C* **3**, 1026 (1970).
- [19] P. Hofmann, K.-H. Jacob, and E. Knözinger, *Ber. Bunsenges. Phys. Chem.* **97**, 316 (1993); E. Knözinger, K.-H. Jacob, and P. Hofmann, *J. Chem. Soc. Far. Trans.* **89**, 1101 (1993); E. Knözinger, K.-H. Jacob, S. Singh, and P. Hofmann, *Surf. Sci.* **290**, 388 (1993).

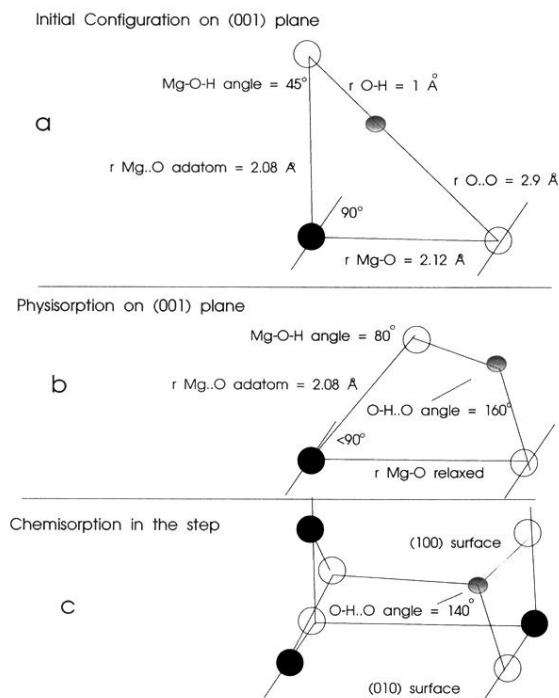


FIG. 3. Schematic drawing illustrating physisorption and chemisorption. Solid circles: Mg atoms; shaded circles: H atoms; and open circles: O atoms. (a) Cut along (010) plane through the initial configuration on the (001) plane. From [19]. (b) Like (a), but after a dynamic run. The O adatom has strongly relaxed thereby reducing the O···O distance across the H atom to 2.6 \AA and the O-H···O angle to 160° . (c) Cut through the step geometry parallel to the (100) surface. The O adatom is coordinated to two Mg atoms, the H atom is influenced by a second O atom. The O-H···O angle is 140° , the resulting H bond is weaker than in (b).