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# DFT study of the water/MgO(100) interface in acidic and basic media

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## Abstract

Periodic-DFT has been used to study the acid–base properties of MgO(100) layers interconnected with an ice filling. The insertion of HCl by substitution of one water molecule shows that all the protons are adsorbed on the surface oxygen atoms forming hydroxyl groups; the  $\text{Cl}^-$  ions are weakly bound to surface cations, generating a monolayer with the adsorbed water molecules. For the insertion of NaOH also by substitution of one water molecule, it is found that  $\text{OH}^-$  ions remain in solution close to the  $\text{Na}^+$  ions, forming ion pairs or chains. Depending on the number of water molecules present, the sodium ions are bi-, tri- or tetra-coordinated. Finally, some aspects concerning corrosion have been highlighted.

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**Keywords:** DFT; MgO; Adsorption; Water dissociation; HCl; NaOH

## 1. Introduction

Pure water at the contact of MgO has been supposed to remain molecular by some authors and to dissociate by others. According to Henderson [1], MgO(100) represents one of the two most controversial cases. From experiments [2–5] it is generally considered that “magnesium oxide surface (100) dissociates water to give rise to highly hydroxylated surfaces” [5] and an estimate of the number of dissociated molecules per surface area has been given. The hydroxyls are mostly located on adsorbing sites that have five-coordinated ions even if dissociation might occur on the corners being followed by hydroxyl migration on terraces. On the other hand quantum chemical calculations [6–17] mostly agree in predicting that the perfect (100) faces do not dissociate water. Therefore it is supposed that

dissociation occurs on defects [6,18–21], steps [12], when surfaces are reconstructed [22,23], under pressure [24] or when traces of acids are present [25]. The lack of dissociation on a perfect surface is a consequence of the poor basicity of the surface  $\text{O}^{2-}$  anions, which are fivefold-coordinated and stabilized by a strong Madelung Field; MgO is an insulator with a valence band low in energy. Most of the adsorbates bind to the surface cations, and in anhydrous conditions the metal surface is predominantly acidic. The presence of water can modify the surface properties and reveal basic properties.

HCl dissociates in liquid water and partially within bulk-ice [26–29]. Interaction between ice and HCl is responsible for pollution phenomena in polar stratosphere [30–33]. It is less clear whether HCl dissociates on ice-surfaces. Two mechanisms have been proposed: either the HCl molecule adsorbs on the surface (forming eventually dihydrates or dissociating [34–40]) or it penetrates inside the ice structure at least in the upmost layers (see Refs. [12–15] in [27] and Refs. [41–43]). Experiments have been made to investigate the HCl adsorption on five bilayers of ice

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supported on MgO [40], showing that HCl-dihydrate coexists with ice Ih at 1HCl monolayer ( $T = 220$  K).

There are few studies of coadsorption of HCl with  $H_2O$  on solid surfaces. On Pt(111), the presence of hydronium was suggested [44]. On metal oxides (titania) Bourgeois et al. [25] have found that the hydroxylation is greatly enhanced by traces of fluorine resulting of the pollution of the UHV system by HF used for chemical etching.

NaOH has been chosen to study the basic media because it is the most popular representative.  $Na^+$  has not been observed on defect-free surfaces; it is believed to adsorb only in the vicinity of step edges or kink sites [45]. On NaCl surfaces, the adsorption energy decreases from 0.5 eV to 0.1 eV when water is present at the interface [46].

Modeling the interface between acid and base solution, and metal oxide surface represents a complex system; indeed, it involves three kinds of interactions: those between water and surface, those between the solvated molecule and the surface, and finally those between the solvated molecule and the water. The acid and base easily dissociate into ionic fragments. The interaction which is of interest here, and which must be investigated, is the one of the two ions with the surface and the water media.

In this study, this complex system has been modeled through periodic quantum chemical methods. Since temperature is mostly not taken into account in such methods, water is modeled by ice. Ice is always the structure representing water and results have to be extrapolated to represent a liquid media. Molecular dynamics or Monte-Carlo simulations can provide valuable information (see Refs. [47,48]), however with the known difficulties and drawbacks such as the needed computational power [47,48]. In embedded techniques, the region of the interface is privileged and the liquid perturbs (reduces) mostly the energy without changing much the structures [48]. QM calculations remain a useful tool of analysis, treating the different interactions on equal footing.

## 2. Computational details

We have carried out ab initio periodic calculations with the Vienna Ab initio Simulation Package code [49,50] (VASP 4.4.4). In the VASP program, the Kohn–Sham equations are solved with the generalized gradient approximation (GGA) proposed by Perdew et al. [51,52]. Ultra-soft pseudopotentials have been used [53,54] together with plane wave basis sets. The cutoff of plane waves is 400 eV. The integrations in the Brillouin zone are performed on a grid of  $5 \times 5 \times 1$  for the geometry.

MgO is often chosen as representative for the metal oxides due to its simple structure; the bulk possesses a rock-salt structure with an alternation of ions with opposite charge [55,56].

The (100) surface is stable, nonpolar, classified of type I according to Tasker [57]. The clean surface is easy to prepare with well defined stoichiometry [18], and it does not undergo large relaxations. We have modeled a three-layer thick slab of MgO using a  $\sqrt{2} \times \sqrt{2}$  unit cell with a lattice,  $a (=b)$ , parameter of 4.211 Å taken from the bulk value [58,59]. This value also represents the parameter calculated by VASP for the bulk optimization, 4.2118 Å. The slab is periodically repeated to generate a 3D calculation.

A fixed  $c$  value of 13 Å was chosen, allowing the accommodation of four layers of water molecules without dissociation [24]. For the study of the adsorption of individual molecules this value corresponds to an empty gap of 9 Å.

A slab with the (001) orientation has a square lattice periodicity, allowing a structure in epitaxy over MgO by a small contraction of the lattice parameter of the square unit cell, 4.272 Å [60]. This is compensated by a vertical expansion of the water slab. The epitaxy gives a formal coverage of 1/2 for the first layer of water on the surface. It should be noted that this “sandwich” model, with two surfaces is very suited to model the water oxide interface resulting effectively in a larger surface area.

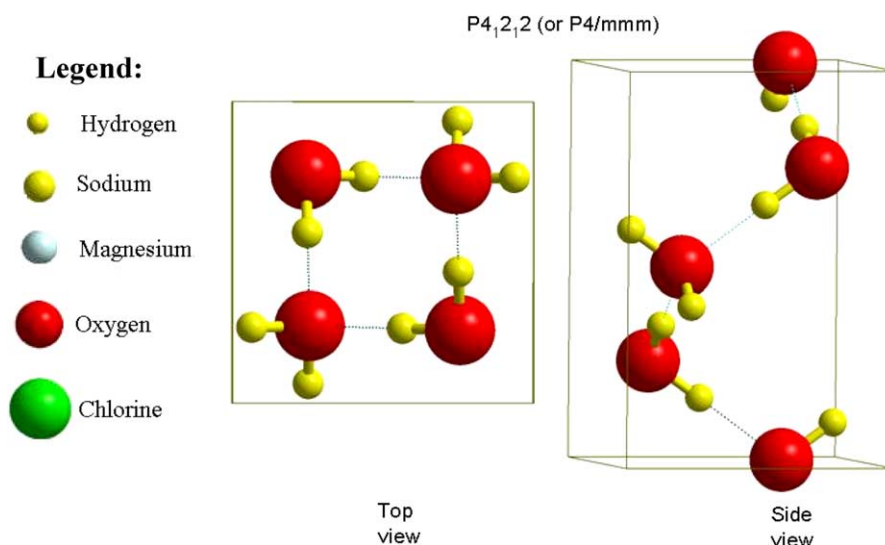


Fig. 1. The unit cell of proton-ordered water P4<sub>1</sub>2<sub>1</sub>2. The legend for the atomic representation in all the figures is provided.

The space between the successive MgO slabs was filled by a slab of proton-ordered water. The cubic ice (water) structure with  $P4_12_12$  symmetry (see Fig. 1), where the sublattice of the O atoms has a FCC structure instead of a HCP one, has been used; it is an antiferromagnetic structure [60].

In these systems, we have replaced a water molecule by an X molecule ( $X = \text{HCl}$  or  $\text{NaOH}$ ). The interspace between the MgO layers then contains one X molecule and three water molecules per unit cell. The energies,  $E_S$ , for these new systems have been defined relative to that of the unsubstituted system (four layers of water molecule in the interspace), and to those of  $\text{H}_2\text{O}$ , and of X molecules according to the expression:

$$\Delta E_S = E(4\text{H}_2\text{O layers inserted}) + [E(X) - E(\text{H}_2\text{O})] - E(\text{system}) \quad (1)$$

The adsorption energies  $\Delta E_{\text{ads}}$  are defined as follows:

$$\Delta E_{\text{ads}} = \left[ E(\text{slab}) + \sum E(Y_i) \right] - E(\text{system}) \quad (2)$$

with  $Y_i = \text{H}_2\text{O}$ ,  $\text{HCl}$  or  $\text{NaOH}$ , yielding positive adsorption energies for exothermic interactions.

All the positions of the atoms were optimized, i.e. the MgO layers as well as the water and/or HCl and/or NaOH. The calculated energies of the isolated molecules are:  $E(\text{H}_2\text{O}) = -14.248$  eV,  $E(\text{HCl}) = -6.057$  eV,  $E(\text{NaOH}) = -11.411$  eV. For water, the distance and angle are  $d_{\text{OH}} = 0.972$  Å and  $106^\circ 4'$ , respectively; for HCl the distance is  $d_{\text{HCl}} = 1.282$  Å, and for NaOH, the distances and angle are:  $d_{\text{NaO}} = 1.995$  Å,  $d_{\text{HO}} = 0.971$  Å, and  $\angle \text{NaOH} = 128^\circ 1'$ , respectively. These values have been calculated using a  $10 \text{ Å} \times 10 \text{ Å} \times 10 \text{ Å}$  box.

### 3. Results and discussion

This manuscript is organized as follows. For each system,  $\text{H}_2\text{O}$ ,  $\text{HCl}$  and  $\text{NaOH}$ , we start by presenting the

adsorption of a single molecule and of the monohydrated species; vacuum is then present in the interspace separating the MgO slabs. Next, we present the system where the interspace is filled by the water. Part a is devoted to  $\text{H}_2\text{O}$ , parts b and c to  $\text{HCl}$  and parts c–e to  $\text{NaOH}$ .

#### 3.1. Water on $\text{MgO}(100)$

As a single molecule ( $\theta = 0.5$ ), water adsorbs very weakly on the MgO surface with an energy slightly better than the energy of a single hydrogen bond, i.e.  $0.47$  eV [61,62].

In this study we have introduced four layers of water with the geometry of  $P4_12_12$  ice (see Fig. 1) in the space between three layers of MgO. After complete optimization for a constant volume, it was found [24] that water does not dissociate and preserves its structure (see Fig. 2). Water binds to the two opposite surfaces of the MgO slab. On the bottom surface, water is adsorbed through H to a  $\text{O}_{\text{lattice}}$  atom while on the upper surface water is adsorbed through an electron pair to a  $\text{Mg}_{\text{lattice}}$  atom. The surfaces of MgO are slightly buckled. On the bottom surface, the  $\text{O}_{\text{lattice}}$  atoms are external and the Mg atoms are  $0.04$ – $0.09$  Å below. On the upper surface, a pair of Mg and O is shifted outward relatively to the other (by  $0.07$ – $0.12$  Å).

#### 3.2. Single HCl and $\text{H}_2\text{O}$ molecules on $\text{MgO}(100)$

##### 3.2.1. HCl molecule

For the adsorption of a single HCl molecule (see Fig. 3), the dissociated form  $\text{H}^+/\text{O}^{2-}$  and  $\text{Cl}^-/\text{Mg}^{2+}$  is the situation of lowest energy (see Table 1), the adsorption preserving the electronic gap [17,63]. For the dissociative chemisorption with  $d_{\text{OH}} = 1.01$  Å and  $d_{\text{Mg-Cl}} = 2.35$  Å an adsorption energy of  $E_{\text{ads}}(\text{HCl}) = 0.54$  eV is found, which is slightly stronger than for a single water molecule. The strong interaction between the ions and the surface is partially

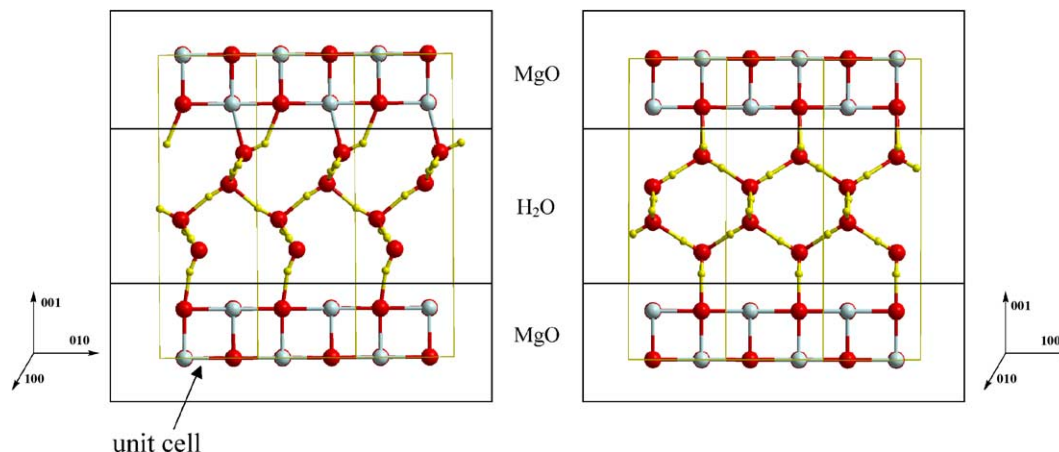


Fig. 2. The four layers of proton-ordered water (seen along the  $(100)$  direction of the  $P4_12_12$  bulk unit cell) epitaxially inserted in three-layer MgO slabs. The water structure is preserved in the optimization. The water molecules are bound to the lower surface as Brønsted acids and to the upper surface as Lewis bases.

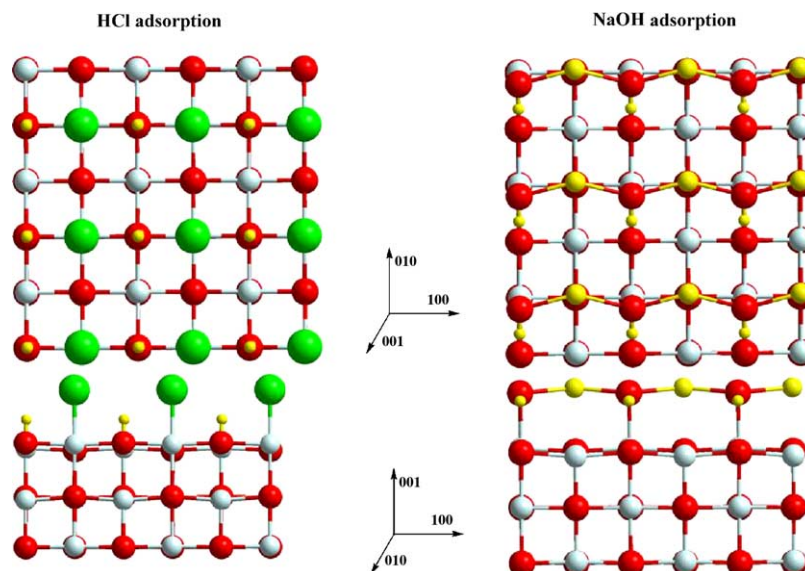


Fig. 3. Optimized structures for HCl and NaOH adsorption at  $\theta = 1/2$  in vacuum.

Table 1

Adsorption energy (eV) of HCl and  $\text{H}_2\text{O} + \text{HCl}$  molecules (positive for exothermic processes)

Adsorbate	$\Delta E_{\text{ads}}$ (eV)
HCl dissociated	0.54
HCl physisorbed	0.43
HCl dissociated + $\text{H}_2\text{O}$ molecular	1.63
HCl dissociated + $\text{H}_3\text{O}^+$	1.03–1.02

The reference energy is the sum of the energies for the slab and for the individual molecules.

balanced by the cost for the cleavage of the HCl bond, so this value is less than that one might think. The final system contains  $\text{OH}^-$  groups at the surface which is the consequence of the neutralization of HCl by MgO; the basic property of the surface is revealed by the adsorption of a strong acid. The molecular physisorption without dissociation and with an orientation approximately perpendicular to the surface, H-down above surface oxygen, is slightly weaker  $E_{\text{ads}}(\text{HCl}) = 0.43$  eV. The physisorption has also been investigated using periodic HF calculations [47] yielding 0.24 eV (0.48 eV after correlation correction). Our corresponding value calculated with VASP is 0.28 eV. The adsorption geometry has also been determined by modeling photolysis experiments of HCl on MgO [64,65].

### 3.2.2. Coadsorption ( $\text{HCl} + \text{H}_2\text{O}$ )

We have also calculated the coadsorption of HCl with  $\text{H}_2\text{O}$  (one molecule of each per  $\sqrt{2} \times \sqrt{2}$  unit cell). The same unit cell was used to study the coadsorption of one HCl molecule with one  $\text{H}_2\text{O}$  molecule (see Fig. 4a). The structure with the complete dissociation of the two molecules evolves, during the optimization process, to the adsorption of a molecular  $\text{H}_2\text{O}$ , being the geometry of lowest energy. Only HCl dissociates with again the formation of a surface hydroxyl group. The adsorption energy re-

ferred to the two independent molecules is 1.63 eV, which is much better than the sum of both molecules separately. The  $\text{Cl}^-$  and the water molecules form chains stabilized by H-bonds. The formation of a hydronium ion bound to the surface is less favorable; both modes (hydronium ion bound to  $\text{Mg}^{2+}$  by the O pair or to  $\text{O}^{2-}$  through an H-bond) are isoenergetic,  $E_{\text{ads}} = 1.02$ –1.03 eV. For these structures, the chloride ion is only weakly bound to the surface  $d_{\text{Mg-Cl}} \sim 3.2$  Å. The main conclusion is that the proton generated by the HCl cleavage binds preferentially to the surface O atoms forming hydroxyls (see Fig. 4a) than to water forming hydronium ions. Water does not dissociate. The hydronium ions may be formed when all the O atoms are already covered, the oxygen pairs of the water molecules being only accessible; however they should not appear at low coverage.

### 3.3. HCl in water between MgO slabs

The unit cell now contains three water molecules, and one HCl molecule in the interspace between the MgO layers (see Fig. 5). The energy of the system is defined by the exchange of a HCl molecule with a water molecule between the system and the gas phase; it is referred relatively to the interface containing pure water, and a HCl molecule in the gas phase as explained in Section 2 (see Eq. (1)). In pure water [27], HCl dissociates and the proton migrates to form an  $\text{H}_3\text{O}^+$  with the molecules second neighbor relative to the  $\text{Cl}^-$  ion.

When HCl is placed within the water system of the MgO interspace, it also dissociates. In the most stable topologies, the  $\text{Cl}^-$  ions form with water molecules a monolayer, while the  $\text{H}^+$  ions bind to the lattice oxygen and form  $\text{OH}^-$  ions. It is again a neutralization of HCl by the MgO surface. All of the protons are consumed by the surface  $\text{O}^{2-}$  ions and none is left in the solution that consists of water molecules



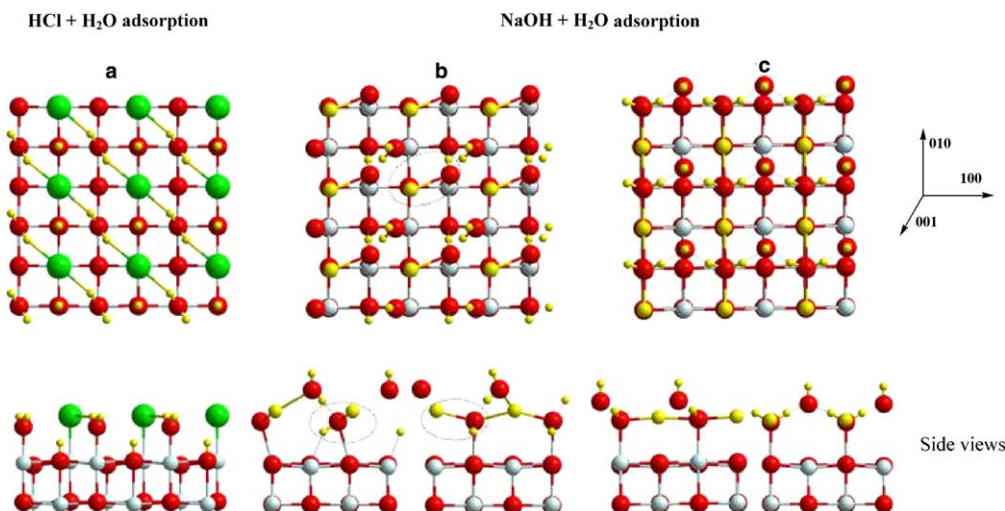


Fig. 4. Top view and side views of the optimized structures for coadsorption in vacuum of HCl and H<sub>2</sub>O molecules, and NaOH and H<sub>2</sub>O molecules.

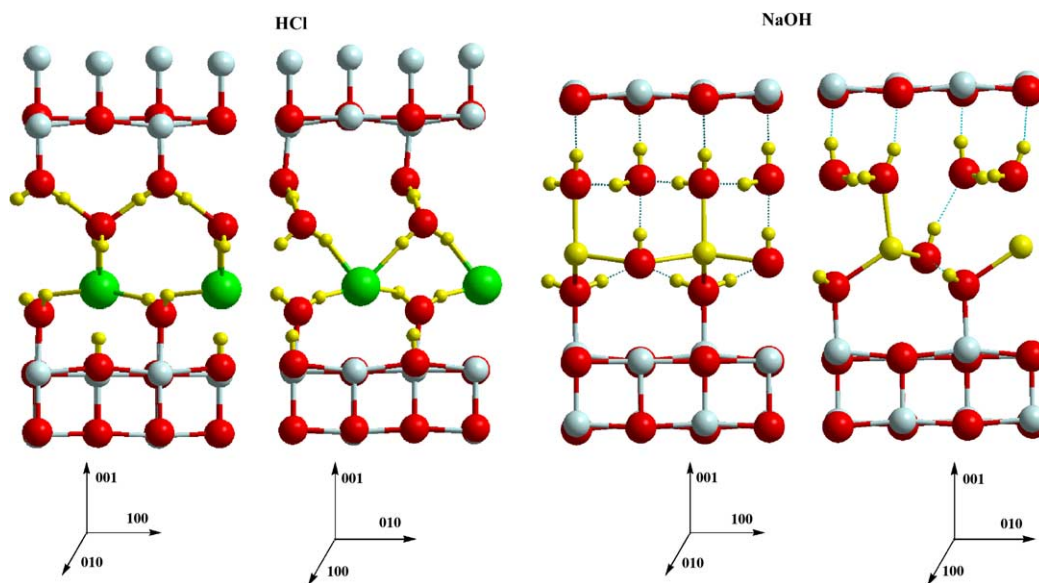


Fig. 5. Side views along the (100) and (010) direction of the optimized structure of lowest energy for HCl and NaOH insertion. Left: The Cl<sup>−</sup> ion is at 2.94 Å of the surface Mg atom, at 2.02–2.08 Å of the hydrogen atoms from the water above and at 2.22–2.32 Å of the hydrogen atoms from the water below. Right: The Na<sup>+</sup> ions are coordinated to 2OH<sup>−</sup> and one H<sub>2</sub>O. The OH<sup>−</sup> are stabilized by 2H-bonds and 2Na<sup>+</sup>.

and Cl<sup>−</sup> ions. In our model, there is one HCl molecule per four surface oxygen atoms (two surfaces and a  $\sqrt{2} \times \sqrt{2}$  unit cell) and most of the surface oxygens remain uncovered. We are therefore far below the situation where all of them would be turned into hydroxyl which represents a passivated surface. Over this limit, the H<sup>+</sup> ions would still not stay in solution but would bind to the surface hydroxyls forming water; this would erode the surface and the Mg<sup>2+</sup> surface-ions remaining alone on the surface could trap the chlorides ions forming MgCl<sub>2</sub> and inducing strong corrosion.

Energies for the different adsorption modes that we have calculated are gathered in Table 2. When the H<sup>+</sup> ions bind to the same surface than the Cl<sup>−</sup> (Fig. 5), the process is exothermic by  $\Delta E_S = 0.45$  eV; when they bind to the opposite

surface the energy gain is slightly reduced,  $\Delta E_S = 0.40$  eV. The MgO surfaces are buckled, all the sites bound to adsorbates being attracted outward: For the surface below, the O<sub>lattice</sub> of the hydroxyl groups and the Mg atoms bound to the water molecules are shifted up. The binding of the chloride ions to Mg is weaker than that of the H<sup>+</sup> to the O atoms of the surface. So, that the surface Mg atoms remain below the average surface plane. For the surface above, the Mg atoms bound to the water molecules or the protonated oxygen atoms (on the upper surface) are shifted down.

We have also obtained a stable configuration exchanging the Cl<sup>−</sup> layer with the water layer beneath, bringing the Cl<sup>−</sup> close to the surface and moving the water molecules outward. The buckling of the surface layer is reversed

Table 2

Energy  $\Delta E_S$  (eV) as defined in Eq. (1) for the substitution of HCl for H<sub>2</sub>O in the interspace filled with water (positive values for exothermic processes)

Adsorption site	Main interaction	$d_{\text{MgCl}}$ (Å)	$\Delta E_S$ (eV)
Cl in ice, H adsorbed on same surface	Cl <sup>−</sup> /H <sub>2</sub> O and H <sup>+</sup> /O <sub>surf</sub>	2.94	0.45
Cl in ice, H adsorbed on opposite surface	Cl <sup>−</sup> /H <sub>2</sub> O and H <sup>+</sup> /O <sub>surf</sub>	2.89	0.40
H and Cl adsorbed on opposite surfaces	Cl <sup>−</sup> /H <sub>2</sub> O and H <sup>+</sup> /O <sub>surf</sub>	2.40	0.15
Cl solvated + H <sub>3</sub> O <sup>+</sup>			−1.21
H and Cl adsorbed on same surface	Cl <sup>−</sup> /Mg <sub>surf</sub> and H <sup>+</sup> /O <sub>surf</sub>	2.44	−0.41
Cl in surface plane + 2OH			−2.03

The distances of the chlorine atom to the Mg<sub>lattice</sub> is indicated; the Mg–Cl distance in MgCl<sub>2</sub> is 2.18 Å; above 2.5 Å, the interaction between Mg and Cl is weak.

to enhance the interaction with chloride ions closer to the surface. The proton is adsorbed on the opposite surface than the Cl. The energy of the system is slightly weaker,  $\Delta E_S = 0.15$  eV.

The system where H<sup>+</sup> is bound to a water molecule and forms a hydronium cation is a secondary minimum high in energy and endothermic ( $\Delta E_S = -1.21$  eV using the definition from Eq. (1)). The O<sup>2−</sup> atoms of the surface are much more basic than the O atoms from water and thus H<sup>+</sup> naturally reacts better with them to form OH<sup>−</sup>. This leaves the surface layer charged and with an unbalanced stoichiometry (MgOH<sup>+</sup>) which should be a step toward the formation of Mg<sup>2+</sup>(H<sub>2</sub>O) with another HCl molecule that could react with Cl<sup>−</sup>; forming magnesium chloride and peeling thus the first layer. Corrosion would then easily happen layer by layer.

Finally, the penetration of the Cl<sup>−</sup> has been investigated, which represents another mechanism for corrosion. First, we have adsorbed the two ions resulting from the HCl dissociation on the same surface: H<sup>+</sup>/O<sup>2−</sup> and Cl<sup>−</sup>/Mg<sup>2+</sup>. The three H<sub>2</sub>O molecules form a homogeneous structure above; this structure is endothermic ( $\Delta E_S = -0.41$  eV). The distance between the H and the Cl is 1.906 Å which corresponds to HCl dissociation into adjacent ion pairs. Next referring to the structure described in Fig. 2, an O from the surface has been substituted by a Cl atom and one proton has been removed from the water layers for charge neutrality. The new system contains the same atoms per unit cell than the previous ones and corresponds to the initiation of the penetration of Cl<sup>−</sup>; indeed, the optimized structure represents the initial step for an exchange between a Cl<sup>−</sup> anion and an OH<sup>−</sup> hydroxyl from the surface leading to corrosion of the oxide. The system is strongly endothermic  $\Delta E_S = -2.03$  eV; the solution splits into two parts. A water

molecule is dissociatively adsorbed on the unsubstituted surface and stabilized by a molecular water layer. The substituted surface that has a mixed composition between a chloride and an oxide is stabilized by a single water molecule. This mechanism for corrosion is therefore unlikely.

### 3.4. NaOH in pure water

As a matter of completeness and in line with our former study of the ionization of HCl in ice [27], we have investigated the behavior of one NaOH molecule in ice. The calculation strategy and level is described elsewhere [27]. The reaction energy for the substitution process NaOH + ice → ice-NaOH + H<sub>2</sub>O is exothermic,  $\Delta E_S = 0.84$  eV.

In contrast with HCl, which dissociates in ice, NaOH does not, but forms tight ion pairs. The closest oxygen atoms to the sodium ion are situated in a distance range between 2.18 and 2.36 Å, i.e. an enlargement of 10% of the Na–O bond (see Table 3). Na is tricoordinated; it is bound to two water molecules whose orientation remained unaffected through the optimization (see Fig. 6) preserving the ice structure. To our knowledge, the only quantum calculation on similar system was made by imposing the position of Na [66].

### 3.5. Single NaOH and H<sub>2</sub>O molecules on MgO(100)

#### 3.5.1. NaOH molecule

For the adsorption of a single NaOH molecule (see Fig. 3), the most stable geometry corresponds to chains of alternate ions Na<sup>+</sup> and OH<sup>−</sup>. The Na–O distance (Table 3) is similar to that in the tight ion pair in pure ice (see Section 3.4). With a value of  $\Delta E_{\text{ads}} = 2.18$  eV, this adsorption energy is almost four times stronger than that of an HCl molecule.

Table 3

Shortest NaO distances (Å) for the NaOH insertion into the different systems considered

Gas phase	Pure water	Adsorption on MgO	Coadsorption with H <sub>2</sub> O on MgO (Fig. 4b)	Coadsorption with H <sub>2</sub> O on MgO (Fig. 4c)	Water between MgO slabs
1.95 (OH)	2.18 (OH)	2.17 (OH)	2.28 (OH)	2.51 (OH)	2.39 (OH)
	2.29 (H <sub>2</sub> O)	2.17 (OH)	2.35 (OH)	2.55 (OH)	2.41 (OH)
	2.36 (H <sub>2</sub> O)	2.50 (O <sub>lattice</sub> )	2.47 (H <sub>2</sub> O)	2.07 (H <sub>2</sub> O)	2.23 (H <sub>2</sub> O)
				2.15 (H <sub>2</sub> O)	2.31 (H <sub>2</sub> O)

Na–O bond distance in gas phase: 1.950 Å; both in this work and experiment [67]. In parenthesis is indicated whether the O from the Na–O bond pertains to a hydroxyl, a water molecule or the lattice.

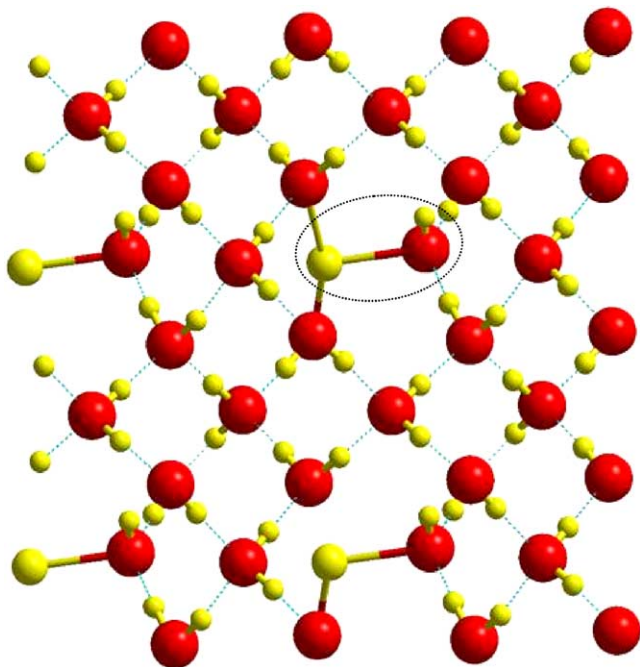


Fig. 6. Optimized NaOH ion pairs in ice. The NaOH is shown within a circle.

### 3.5.2. Coadsorption ( $\text{NaOH} + \text{H}_2\text{O}$ )

In parallel with the HCl study, we have also optimized the  $\text{NaOH} + \text{H}_2\text{O}$  coadsorption on  $\text{MgO}(100)$  (see Fig. 4b and c, one molecule of each in a  $\sqrt{2} \times \sqrt{2}$  unit cell). We have found two adsorption modes, very close in energy,  $\Delta E_{\text{ads}} = 3.04$  eV and 2.97 eV. Interesting to note is that these adsorption energies are better than the sum of both molecule ( $\text{H}_2\text{O}$  and  $\text{NaOH}$ ) separately ( $0.47$  eV +  $2.18$  eV =  $2.65$  eV). In the first one, the NaOH is bound to the surface through the O atom and  $\text{H}_2\text{O}$  forms the second layer. In the first one (Fig. 4b), NaOH does not dissociate and water stays molecular ( $3.04$  eV). The water molecule is linked to NaOH via hydrogen bridges and Na–O bonds. The sodium is essentially tricoordinated (see Fig. 4b). The elongation of the Na–O bond until  $2.28$  Å (an increase of 18%) corresponds to the formation of an ion pair (Table 3).

The second one (Fig. 4c) corresponds to  $\text{H}_2\text{O}$  adsorption, NaOH being dissociated. The Na–O distance is larger than  $2.5$  Å (Table 3). The  $\text{Na}^+$  is bridging two water molecules forming rows ( $d_{\text{Na-O}} = 2.07$  and  $2.15$  Å). The  $\text{OH}^-$  ions are stabilized by four interactions, two with the sodium cations and two H-bonds with the water molecules.

These results show that, from the different geometries possible, it is better to bind the OH from NaOH or  $\text{H}_2\text{O}$  to the  $\text{Mg}^{2+}$  than to link the sodium to oxygen atoms of the MgO surface. The situation where  $\text{Na}^+$  is also bound to the surface corresponds to  $\Delta E_{\text{ads}} = 2.62$  eV;  $\text{Na}(\text{OH})_2$  is then bound to three surface atoms while the forth in the unit cell is protonated.

Table 4

Energy  $\Delta E_{\text{S}}$  (eV) as defined in Eq. (1) for the substitution of NaOH for  $\text{H}_2\text{O}$  in the interspace filled with water (positive values for exothermic processes)

Adsorption mode	$\Delta E_{\text{S}}$ (eV)
Ion pairs in ice forming chains	1.94
NaOH and $\text{H}_2\text{O}$ without dissociation	1.34
The Na from NaOH is adsorbed on $\text{Mg}_{\text{surf}}$	
NaOH without dissociation and $\text{H}_2\text{O}$ with dissociation	1.33
The two atoms from NaOH are adsorbed	
NaOH with dissociation and $\text{H}_2\text{O}$ without dissociation	1.12
The Na is bound to $3\text{H}_2\text{O}$ and OH is adsorbed on $\text{Mg}_{\text{surf}}$	
Exchange Na–Mg	0.43
Insertion between MgO layers	−3.5

### 3.6. NaOH in water between MgO slabs

NaOH dissociates within the water system of the interspace between the MgO slabs (see Fig. 5 and Table 4). The energy of the system referred to the molecules,  $\Delta E_{\text{S}} = 1.94$  eV, corresponds to a highly exothermic process. The  $\text{Na}^+$  cations are fourfold-coordinated (Table 3); indeed, they form chains of ions with the  $\text{OH}^-$  (two neighbors) and are firmly bound to two water molecules. The O atoms from  $\text{OH}^-$  are stabilized by two H-bonds in addition to the two  $\text{Na}^+$ . This situation is close to that described in Fig. 4c for the coadsorption. The NaOH thus interacts with the water and not directly with the surface. MgO however contributes to modify the insertion mode of NaOH that differs from that in pure ice; this is because it stabilizes the ionic contributions in the ice. Note that the water media is also necessary to allow NaOH dissociation that did not occur with the same extent for the coadsorption (see Section 3.5, above). The NaOH dissociation is also revealed by the Na–O distances; these are longer for the hydroxyls than for the neighboring water molecule (Table 3).

The situations where NaOH is closer to the surface are energetically less favorable,  $\Delta E_{\text{S}} = 1.1$ – $1.3$  eV (Table 4).

The substitution of an Mg atom of the surface by a Na is relatively unfavorable. In this case  $\text{Na}^+$  alternate with hydroxyl groups in the “surface” layer while  $\text{Mg}^{2+}$  in the solution is bound to two  $\text{OH}^-$ . Cations,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , remain in interaction with  $\text{OH}^-$  ions. Finally, the insertion between the surface and the sublayer is strongly endothermic ( $\Delta E_{\text{S}} = -3.5$  eV).

The main conclusion from these calculations is that the largest interaction concerns the ion pairs forming chains within the water phase. These ions do not interact directly with the surface; however the presence of the MgO contributes to stabilize the charged species and favors the dissociation.

## 4. Conclusions

Periodic density-functional theory calculations have been performed on HCl/water and NaOH/water filling the interspace between  $\text{MgO}(100)$  slabs.



It was found that HCl dissociates in the aqueous/water solution;  $\text{Cl}^-$  remains in solution while  $\text{H}^+$  is adsorbed on the surface oxygen atoms. The adsorbed protons form at first hydroxyl groups and next, under saturation, water. When the number of protons available in solution is less than half of the number of surface oxygen atoms, no proton is left in solution. Under this number (50% of the surface oxygen sites), the hydroxylated top layer is stable. Beyond this number, the surface hydroxyls start to be protonated, generating water molecules and the surface layer appears as if it was made of solvated  $\text{Mg}^{2+}$  ions, which can easily capture chloride ions. The insertion of  $\text{Cl}^-$  within the oxide structure is found to be expensive.

For NaOH, the  $\text{Na}^+$  and  $\text{OH}^-$  ions remain in interaction; NaOH does not dissociate in pure ice, but forms compact ion pairs. When the MgO surface is present (coadsorption or interface with ice) it forms ion pairs or chains. In the most stable structures investigated, the sodium cations are bi-, tri- or tetra-coordinated. Surprisingly, there is no surface hydroxylation (OH bound to surface Mg atoms). However the presence of MgO surface contributes to facilitate the NaOH dissociation.

Under hydration conditions, the oxide surface reveals high basic properties which do not appear in vacuum where the reactivity of surface cations predominates. The protonation of the surface oxygens when HCl is present is a neutralization of the acid by a basic surface. The mechanism for corrosion starts by this process. On the contrary, the penetration of the chlorine (substitution or insertion) in the MgO layers is endothermic.

## 5. Supplementary materials

Colored figures and additional ones are available on the web site: <http://www.lct.jussieu.fr/minot/water.html>.

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