The water adsorption on the surfaces of SrMO$_3$ (M= Ti, Zr, and Hf) crystalline oxides: quantum and classical modelling

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Abstract. Hybrid HF-DFT LCAO simulations of (001) surface properties and water adsorption on cubic SrTiO$_3$, SrZrO$_3$, and SrHfO$_3$ perovskites are performed in a single-slab model framework. The optimized atomic structures and water adsorption energies have been calculated for a single water molecule per the surface unit cell. The possibility of the water molecular dissociation was investigated. Basing on the experimental data and results of the ab initio calculations the new interatomic potentials have been developed to describe the bulk and surface properties of the binary and ternary titanium and zirconium oxides. The proposed force-field takes into account the polarization effects via the shell model. The force-field suggested was used in the molecular mechanics calculations with the extended unit cells to study the possible surface reconstruction upon relaxation and hydroxylation of cubic perovskites.

1. Introduction

The bulk and surface electronic structure of transition metal oxides with a perovskite lattice have attracted much attention due to their optical and electronic properties and their catalytic activity. One such family of oxides is represented by the formula SrMO$_3$, where M is the IV-group metal. The solid state chemistry of these perovskite-type compounds is very interesting from the theoretical point of view, because the relation between the physical properties and the chemical characters (ionicity, polarizability, equilibrium length, etc.) of M–O bonds is not understood completely. Till now a number of experimental [1–4] and theoretical [5–7] studies of pure and hydroxylated SrTiO$_3$ (001) surfaces have been reported. In contrast, the surface properties of SrZrO$_3$ and SrHfO$_3$ are investigated to a much less extent (see Ref. [8–12]).

It is now widely recognized that computer modelling techniques are well established tools in the field of materials chemistry, and have been applied successfully to studies of structures, energetics and dynamics of solids at the atomic level. In the past few years, first-principles methods have made an increasingly significant contribution to understanding the nature of crystal bulk and surface properties. However, some theoretical problems cannot be solved using the models based on the small-size bulk or surface unit cells. Thus, study of many-layer molecular adsorption on the crystal surfaces, calculation of statistical distributions and treating the temperature effects require the large-scale simulations that yet are not possible on an ab initio level. Just a combination of the quantum
mechanical methods and the classical force-fields forms an approach which gives the possibility to extend the results of \textit{ab initio} calculations to large-scale systems.

In this paper, we present molecular modeling results for surface properties of strontium perovskites obtained via the \textit{ab initio} calculations. Basing both on these results and the available experimental data the new set of interatomic potentials has been developed to describe the bulk and surface properties of the binary and ternary titanium and zirconium oxides. The proposed force-field takes into account the polarization effects via the shell model. The force-field suggested was used in the molecular-mechanics calculations with the extended 2D unit cells to study the possible surface reconstruction upon relaxation and hydroxylation of cubic strontium perovskites.

2. Computational details

2.1. Quantum mechanical calculations

In this work the hybrid Hartree-Fock – Density Functional Theory (HF-DFT) method using the linear combinations of atomic orbitals (LCAO) was applied for the simulations of the surface properties and water adsorption on the SrZrO$_3$, SrTiO$_3$, and SrHfO$_3$ (001) surfaces. We have applied the CRYSTAL-2003 [13] computer code as a tool for exploring surface properties using the two-periodical single-slab model. We have chosen the B3LYP [14] exchange-correlation functional because it had been successfully applied both for the calculation of SrTiO$_3$ bulk and surface properties [6] and for study of the water-oxide interactions [15]. The small-core Hay-Wadt pseudopotentials [16] for Sr, Ti, Zr, and Hf atoms were used. The modified Hay-Wadt atomic basis sets [17] were adopted for Sr, Ti, and Zr. In the case of Hf we removed the most diffuse exponents (< 0.15) from the original set. The all-electron basis set [18] was used for oxygen and hydrogen atoms. The Monkhorst-Pack [19] 6×6 net was used in the two-dimensional Brillouin zone sampling. No basis set superposition errors (BSSE) were taking into account on this stage of calculations. The BSSE for regarded systems can be estimated from our previous work [9]: it is about 0.1 J/m$^2$ for the surface energy, and about 12 kJ/mol for the water adsorption energies.

To provide the more reliable estimation of surface atomic relaxations and adsorption energies, the lattice constant $a$ of the cubic bulk unit cell of all regarded crystals was optimized. Obtained lattice constants numerical values are 3.937 Å, 4.191 Å and 4.142 Å for SrTiO$_3$, SrZrO$_3$, and SrHfO$_3$, correspondingly. The B3LYP form of exchange-correlation functionals slightly underestimates (by 1-2 %) the bulk unit cell dimensions: the experimental values of the lattice constant are 3.900 Å [20] for SrTiO$_3$, 4.154 Å [21] for SrZrO$_3$ and 4.114 Å [22] for SrHfO$_3$. However, it is seen that the applied method reproduces correctly the variation of lattice constant in regarded series. Theoretical values of the lattice parameters were applied for all subsequent slab calculations. In Table 1 we compare the bulk and surface properties of perovskites calculated by the different \textit{ab initio} methods.

| Property | SrTiO$_3$ | SrZrO$_3$ | SrHfO$_3$ |
|----------|-----------|-----------|-----------|
| $E_S$ (J/m$^2$) | This work | Literature data [PW-LDA$^a$] | This work | Literature data [PW-LDA$^a$] | This work | Literature data [FLAPW-LDA$^b$] |
| BG (eV) | | | | | | |
| BG exp. | 3.65 | 1.85 [5] | 5.02 | 3.62 [10] | 5.80 | 3.67 [12] |

\textsuperscript{a}Linear-density approximation on the plane-wave basis set.
\textsuperscript{b}Linear-density approximation using the linearized augmented plane waves.
According to different possible types of terminating of (001) perovskites surface, two slab models have been used in our calculations. The first one (I) corresponds to SrO-terminated surface and the second one (II) - to Mo$_2$O$_5$-terminated surface. Both models consist of the odd number of atomic planes being symmetrical with respect to the central mirror plane but nonstoichiometric. Models I and II have been applied for studying the surface properties of titanates in the previous *ab initio* calculations [5–9]. As follows from Ref. [6, 9], the consideration of the 7 atomic plane slabs is sufficient for convergence of the calculated surface properties.

2.2. Classical force-field calculations.

Atomistic simulations are based on the Born model of solids [23] which assumes that the ions interact via long-range electrostatic forces and short-range forces which can be described using simple analytical functions. The components of the short-range forces include both the repulsions and the van der Waals attractions between electron charge clouds of neighboring atoms. The Buckingham, Lennard-Jones, or Morse potentials are most frequently used to describe the short-range contributions. The Coulombic interactions are summed using the Ewald method [24] for three-dimensional periodic systems, such as bulk crystals, or the Parry method [25] in the case of two-dimensional periodicity, e.g., surfaces. The model potential of a system (force field) is defined by the set of charges and the short-range potential parameters needed to describe all interactions between the participating species.

A large number of potential models available for solids include the polarizability of the ions in the system via the shell model of Dick and Overhauser [26]. This shell model describes the ion in a simple mechanical way by a shell of zero mass representing the electronic charge cloud connected to a core containing the entire ion’s mass. The total charge of the ion is the sum of the charges of core and shell. The position of the core represents the position of the ion in the crystal lattice, but the position of the shell has no significance. The shell and core are connected by a harmonic spring with force constant $k$. The short-range forces are assumed to act between the shells, while the Coumblic forces act between all shells and cores except between the core and shell of the same ion. Unlike point-polarizable models which have a fixed polarizability, the shell model allows the polarizability to vary with environment. This provides the applicability of the same shell-core interaction parameters and ionic charges to systems of different structure and composition: bulk, stoichiometric or nonstoichiometric slabs, defects, and so on. That is the main reason why we choose the shell model for classical simulations of bare and hydroxylated perovskites surfaces.

| Crystal    | Lattice parameter $a$, Å | Bulk Modulus, GPa | Static dielectric constant |
|------------|--------------------------|-------------------|---------------------------|
|            | *ab initio*, Force-Field | Experiment        | *ab initio*, Force-Field  | Experiment       | Force-Field | Experiment |
| SrTiO$_3$  | 3.937                    | 3.956             | 3.900–3.905              | 186              | 202         | 183        | 329        | 301        |
| SrZrO$_3$  | 4.191                    | 4.108             | 4.109–4.151              | 162              | 176         | 150        | 25         | 16         |

It should be noted that creating the force field for such heterogeneous system as the oxide-water interface is not a simple task due to presence of physically different types of interactions. By this reason our selecting and adjusting of potential parameters was based on several previous studies both of the bulk perovskites structure [27, 28] and the water-surface interactions [29]. The entire procedure was divided onto four steps: (1) adjusting the ion-ion interaction parameters using the crystal bulk properties; (2) testing the reproducibility of the bare surface properties; (3) choosing the intra- and intermolecular potentials for the water-water interactions; (4) adjusting the potentials for the water-surface interactions. All classical molecular mechanics calculations were made using the GULP [30] computer code.
### Table 3. Parameters for the interatomic potentials

| Parameters | Potentials | Parameters |
|------------|------------|------------|
| Shell harmonic: | $E_i = k_i/2 (r_{i}^{\text{sh}} - r_{i}^{\text{cor}})^2$ | $k_i, \text{eV}$ | Shell charge $q_i, \text{e}$ |
| Sr | 0.000 | 0.000 |
| Ti | 1166.231 | -2.900 |
| Zr | 169.617 | 1.350 |
| O $^b$ | 18.410 | -2.389 |
| O $^w$ | 209.450 | -2.050 |
| General Buckingham: | $E_{ij} = B_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6$ | $B_{ij}, \text{eV}$ | $\rho_{ij}, \text{Å}$ | $C_{ij}, \text{eV} \, \text{Å}^6$ |
| Sr–O | 1045.212 | 0.359 | 0.0 |
| Ti–O | 686.642 | 0.396 | 0.0 |
| Zr–O | 1057.03 | 0.376 | 0.0 |
| O–O $^b$ | 22764.3 | 0.149 | 43.0 |
| Sr–O $^w$ | 686.00 | 0.3333 | 0.0 |
| Ti–O $^w$ | 608.00 | 0.3412 | 0.0 |
| Zr–O $^w$ | 865.00 | 0.3353 | 0.0 |
| O–O $^w$ | 22764.3 | 0.1490 | 28.92 |
| O–H $^c$ | 396.27 | 0.250 | 0.0 |
| General Lennard-Jones 9–6: | $E_{ij} = A_{ij}/r_{ij}^9 - C_{ij}/r_{ij}^6$ | $A_{ij}, \text{eV} \, \text{Å}^9$ | $C_{ij}, \text{eV} \, \text{Å}^6$ |
| Ti–O | 93.8837 | 9.0 |
| Intramolecular Morse $^c$: | $E_{ij} = D_{ij}\{[1-\exp(-\alpha_{ij}(r_{ij}-R_{ij}))]-1\}$ | $D_{ij}, \text{eV}$ | $\alpha_{ij}, \text{Å}^{-1}$ | $R_{ij}, \text{Å}$ |
| H $^w$–O $^w$ | 6.2037 | 2.22 | 0.9238 |
| Harmonic angle bending $^c$: | $E_{ij} = K_{ij} / 2 (\phi_{ij} - \Phi_{ij})^2$ | $K_{ij}, \text{eV}$ | $\Phi_{ij}, \text{deg}$ |
| H $^w$–O $^w$–H $^w$ | 4.20 | 108.69 |
| Intermolecular Buckingham $^c$: | $E_{ij} = B_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6$ | $B_{ij}, \text{eV}$ | $\rho_{ij}, \text{Å}$ | $C_{ij}, \text{eV} \, \text{Å}^6$ |
| H $^w$–O $^w$ | 396.27 | 0.250 | 10.0 |
| Intermolecular Lennard-Jones $^c$: | $E_{ij} = A_{ij}/r_{ij}^{12} - C_{ij}/r_{ij}^6$ | $A_{ij}, \text{eV} \, \text{Å}^{12}$ | $C_{ij}, \text{eV} \, \text{Å}^6$ |
| O $^w$–O $^w$ | 39344.98 | 42.15 |

$^a$ Shell-core parameters from Ref [28].

$^b$ Parameters for O–O interactions from Ref. [27].

$^c$ Parameters for water interactions from Ref [29]; coulomb subtract (50%) has been used for the intramolecular potentials within the water molecule. Core charge of H atom in water molecule: 0.4 e, core charge of O atom in water molecule: 1.25 e.
Seven crystals have been adopted for adjusting of the ion-ion potential parameters: TiO$_2$ (rutile), SrO (cub.), SrTiO$_3$ (cub.), ZrO$_2$ (cub.), SrZrO$_3$ (cub.), SrZrO$_3$ (tetrag.), and SrZrO$_3$ (orthorh.). To fit the parameters values the following reference properties of the bulk crystal were used: the lattice parameters, variable atomic positions, elastic constants and static dielectric constants. The parameters for O-O short-range interactions were taken from Ref. [27], the shell-core interaction parameters for Zr were taken from Ref. [28]. In Table 2 we compare the calculated and observed bulk properties for SrTiO$_3$ and SrZrO$_3$ crystals. It is seen that the deviation of classically calculated properties from experimental data has the same order of magnitude as the differences between the latter and ab initio results. The force-field results for the surface relaxation and hydroxylation are discussed in the next sections. The shell model parameters for the intra- and intermolecular potentials for the water-water interactions were taken from Ref. [29]. The final set of potential parameters is given in the Table 3.

3. Relaxation of (001) surface SrTiO$_3$, SrZrO$_3$, and SrHfO$_3$

3.1. Quantum mechanical calculations
In this work we consider the bare slab systems directly generated from the 3D cubic structure which retains the tetragonal symmetry (P4/mmm). Our results for the atomic relaxation of bare SrTiO$_3$, SrZrO$_3$, and SrHfO$_3$ (001) surfaces are presented in Table 4 together with our force-field results and some literature data. The calculated $\Delta z$ values for the SrTiO$_3$ agree well with vertical atomic displacements found in calculations [6] where almost the same LCAO procedure has been used. The data of LDA PW calculations [5] of SrTiO$_3$ surfaces (not included in Table 4) are also close to ours. Recent DFT study of Wang et al. [12] provided the results for the SrHfO$_3$ surfaces which are very close to ours (see Table 4). Theoretical results indicate that the vertical shifts for the upper Sr atoms are large both in model I and II, though they are negative in the first and positive in the second case (see Figure 1). These shifts on SrO surfaces of SrZrO$_3$ and SrHfO$_3$ are larger than for SrTiO$_3$. Displacements of other atoms are very similar for regarded perovskites, except the inward shift of the top oxygen atom on ZrO$_2$ and HfO$_2$ surfaces which is much greater than the shift of corresponding oxygen atom on TiO$_2$ surface. The X-ray diffraction data [1] for SrTiO$_3$ (001) surface measured at 300 K are presented in the sixth column of Table 4. As well as in other ab initio calculations [5–7], the good agreement between the theory and experiment for SrTiO$_3$ (001) surface was found only for the displacements of the top Sr atoms in the model I. The comparison of calculated and measured displacements for the deeper atoms in SrTiO$_3$ slabs is difficult as the experimental data reveal large average errors. The obvious contradiction between the theory and experiment can be found only in the case of the second layer Ti on the SrO-terminated surface. The experimental study [1] gives a rather large inward shift for this atom which is equal to the shift of superior Sr atom, whereas all known calculations [5–8] including the present ones, give the five-time smaller shift in the opposite direction. The possible reasons for disagreement between theory and experiment are discussed elsewhere [9].

![Figure 1](image-url)

**Figure 1.** Relaxation of the two top atomic layers on the (001) surface of cubic perovskites: (a) SrO-terminated surface; (b) MO$_2$-terminated surface. Large grey balls – oxygen atoms, small dark balls – $d$-element atoms, light grey balls – strontium atoms.
3.2. Classical force-field calculations

To check the reliability of the obtained force-field parameters for the ion-ion interaction we calculated the relaxation of the surface atoms using the same slab models which were used in the \textit{ab initio} calculations. Several sets of parameters obtained by fitting the bulk properties (beginning with different initial parameter values) were tested. The parameter set which gives the best overall reproducing of surface structure was adopted for further calculations. The resulting values of the vertical displacements of the top surface atoms for SrTiO$_3$ and SrZrO$_3$ are shown in Table 4 in comparison with our \textit{ab initio} results and the available experimental data. We can conclude that the proposed parameter set reproduces the surface relaxation of the regarded systems qualitatively correctly.

| Mode 1 | At. plane | Ion | SrTiO$_3$ | SrZrO$_3$ | SrHfO$_3$ | SrO-terminated slabs (M = Ti, Zr, 7-plane models I and II for (001) surface) |
|--------|-----------|-----|-----------|-----------|-----------|---------------------------------------------------------------------|
|        |           |     | \textit{ab initio} | \textit{ab initio} | \textit{ab initio} | \textit{ab initio} | Literature data [12] |
|        |           |     | Force-Field | B3LYP | experiment | Force-Field | B3LYP | experiment | B3LYP | experiment |
| I       | SrO-termin. | 1   | Sr         | -0.12    | -0.22    | -0.25 ± 0.07 | -0.17 | -0.33 | -0.28 | -0.27 |
|         |           |     | O          | 0.05     | 0.01     | -0.3 ± 0.4  | 0.06 | 0.01 | 0.01 | 0.03 |
|         |           |     | M          | 0.07     | 0.06     | -0.24 ± 0.07 | 0.07 | 0.07 | 0.06 | 0.06 |
|         |           |     | O$_2$      | 0.06     | 0.03     | -0.4 ± 0.7  | 0.03 | 0.01 | 0.01 | 0.01 |
| II      | MO$_2$-termin. | 1   | M          | -0.15    | -0.11    | 0.00 ± 0.03 | -0.18 | -0.12 | -0.19 | -0.11 |
|         |           |     | O$_2$      | -0.08    | -0.03    | -0.5 ± 0.3  | -0.09 | -0.12 | -0.17 | -0.12 |
|         |           |     | Sr         | 0.09     | 0.14     | -0.01 ± 0.01 | 0.08 | 0.15 | 0.08 | 0.13 |
|         |           |     | O          | -0.01    | 0.00     | 0.2 ± 0.1   | -0.01 | 0.01 | -0.05 | 0.00 |

4. Water adsorption on perovskite surfaces

4.1. Quantum mechanical calculations

Both possible terminations of cubic perovskites have only one metal ion per primitive unit cell in the surface layer. This means that there is only one electropositive adsorption center per unit cell and respectively only one water molecule can be bonded to the surface by its oxygen atom. At the first stage we consider the adsorption of single water molecule on the metallic adsorption center that corresponds to the half-monolayer coverage. There are two types of water molecular adsorption on (001) surface due to two types of the surface termination and at least four different structures should be regarded for each crystal if the possibility of the water dissociation is taken into account. Actually, the real number of structures to be considered is larger since the different initial structures may lead to different optimized water positions corresponded to various local energy minima. The calculated adsorption energies per one water molecule are given in Table 5 for the most favorable structures.

4.1.1. SrO-termination. Several initial positions of water molecule on the SrO termination of the SrTiO$_3$ surface have been studied. In the most favourable conformation (Figure 2a) the water molecule has the oblique orientation and forms the H-bond with the terminal surface oxygen. The water adsorption energy calculated for this structure is noticeably larger than that obtained with other initial states. This example gives evidence that H-bonding plays an important role in the stabilizing of the water molecule adsorption on the perovskite surfaces.

The simplest way for constructing the initial structure for the dissociative adsorption is to transfer by force a proton in the previously obtained molecular structure along the O–H...O hydrogen bond. However, this approach was unsuccessful in the case of the SrO-terminated titanate surface: during the
optimization the initially dissociative structure returns to the molecular adsorption structure. Thus, we have got an additional conformation of the high stability of the previously retrieved molecular adsorption structure (Figure 2a). Nevertheless, eventually it proved possible to gain the stable dissociative structure starting from another initial state. In dissociative case the oxygen atom of the water molecule shifts to the unit cell boundary and the water protons align with the (010) plane. One of the water protons moves to the surface oxygen and forms an H-bond with the second hydroxyl originated from water. The corresponding adsorption energy turned out to be almost the same as for molecular case showing that both types of adsorption are equally possible on the SrO surface of the SrTiO$_3$.

| Crystal  | Termination | 1/2 monolayer adsorption |   |
|----------|-------------|--------------------------|---|
|          |             | molecular                | dissociative |
| SrTiO$_3$| SrO         | 91.3                     | 91.6          |
|          | TiO$_2$     | 86.8                     | 77.3          |
| SrZrO$_3$| SrO         | unstable                 | 143.1         |
|          | ZrO$_2$     | 79.7                     | 69.7          |
| SrHfO$_3$| SrO         | unstable                 | 134.3         |
|          | HfO$_2$     | 83.9                     | 75.2          |

During optimization of the initially non-dissociative structure with the water molecule attached to Sr atom on SrO surface of the SrZrO$_3$ and SrHfO$_3$, the water molecule spontaneously dissociated producing the structure shown in Figure 3a. The energy of this structure is considerably lower (and the water adsorption energy is larger) than the energy of the other structures considered for SrZrO$_3$ and SrHfO$_3$ (Table 5). Moreover, we could not obtain the stable molecular structure for the half-monolayer adsorption on zirconate and hafniate SrO surface. Consequently, the dissociative adsorption is more favorable on SrO surface of zirconate and hafniate at low coverage, although the dissociative adsorption on SrHfO$_3$ surface is slightly less exothermic than the adsorption on SrZrO$_3$ surface.

**Figure 2.** Molecular adsorption of the one water molecule on SrO-terminated surface of SrTiO$_3$: (a) *ab initio* result; (b) molecular mechanic result with the adjusted potential parameters. Large grey balls – oxygen atoms, small dark balls – d-element atoms, light grey balls – strontium atoms, small white balls – hydrogen atoms.
4.1.2. **MO$_2$-termination.** In the structures chosen for study of the water adsorption on MO$_2$ surfaces the H$_2$O molecule was placed directly above the metal atom. As in the case of the SrO-termination, several initial orientations have been regarded. However, the final optimized structures (Figure 4a) proved to be similar, with the water molecule stooping down to the surface oxygens by its one hydrogen. The absolute energy values for Zr – H$_2$O interactions are slightly lower (by $\approx 4$ kJ/mole) than those for Ti – H$_2$O interactions (see Table 5), whereas for Hf– H$_2$O it is the same. The distance between the water oxygen and top Zr (2.45 Å) or top Hf (2.40 Å) atom is noticeably greater than Ti-O$_w$ distance, 2.26 Å.

Starting with the broken water molecule on the MO$_2$-terminated (001) surfaces of SrZrO$_3$, SrTiO$_3$, and SrHfO$_3$ we have obtained the stable dissociative structures where one of the water protons is moved to the surface oxygen (Figure 3b) and the two created hydroxyl groups are in the trans-position to each other. The adsorption energies (Table 5) for the dissociative structures are lower by 10 kJ/mole than that for the molecular adsorption on the same termination, and considerably lower than energy for the dissociative adsorption on SrO surfaces. This indicates that dissociation of water on MO$_2$ surfaces should be unfavorable in accordance with the available experimental and theoretical data [11]. In Figure 3b it is clearly seen that MO$_2$ atomic plane is crumpled due to the considerable vertical displacements of oxygen atoms upon the hydroxylation. Also, it is interesting to note, that the length of M–O bonds in hydroxyls attached to MO$_2$ surfaces are shorter by 0.1 Å than analogous bonds on SrO surfaces, thus pointing to the more ionic nature of hydroxyls on SrO-terminated surfaces.

4.2. Classical simulations

*Ab initio* optimized molecular adsorption structures were used for adjusting the potentials for the water-surface interactions. Only three parameters (Buckingham $B_{ij}$ for Sr–O$_w$, Ti–O$_w$, and Zr–O$_w$ interactions) were fitted and the other potential parameters for the water atoms were taken from Ref. [29] without any change. Obtained set of parameters was able to reproduce in general the minimum-energy structures of the hydroxylated surfaces of SrTiO$_3$ and SrZrO$_3$. Moreover, proposed force field gives the distances Sr–O$_w$, M–O$_w$, O–H$_w$, and M–O, which are very close to those calculated by *ab initio* method for optimized structures. As can be seen in Figures 2 and 4, in the case of SrTiO$_3$ the agreement is excellent.

The developed force-field has been applied for optimization of the positions of water molecules on the surfaces of SrTiO$_3$ and SrZrO$_3$ crystals using the extended surface unit cell and 9-plane slabs. *Ab initio* calculations are time-consuming for all the systems under consideration. However, we plan to recalculate some of the obtained low-energy structures by *ab initio* method to validate the force-field results.

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**Figure 3.** Dissociative adsorption of the one water molecule on SrO-terminated (a), and HfO$_2$-terminated (b) surfaces of SrHfO$_3$, *ab initio* result. See Figure 2 for the atoms tints.
The use of the extended unit cell allows one to obtain the structures of adsorption layer which cannot be achieved using the primitive surface unit cell of cubic structure. Thus, when the primitive surface cell is used at the half-monolayer coverage, all the adsorbed water molecules are translation-equivalent, whereas in the case of $\sqrt{2}\times\sqrt{2}$ supercell this is not so. As expected, the distortion of the cubic structure surfaces was observed in some cases. It was found that the largest displacements of surface oxygen atoms take place at the low water coverage for the SrO-terminated surfaces. The most prominent zigzag structure was found for the half-monolayer water adsorption on SrO surface of SrZrO$_3$. This gives evidence for the possible surface transformation and reconstruction upon relaxation and hydroxylation of cubic perovskites.

5. Conclusions
1. For all the considered crystals and types of termination the first water molecule (half-monolayer coverage) in each 2D-cell is adsorbed on the metallic atoms (Sr, Ti, Zr and Hf). However, the H$_2$O molecule on the SrO surfaces is noticeably shifted towards the surface oxygen due to its strong interaction with the water H atom. The latter structure favors the formation of hydroxide anions via the water dissociation. As a result the water dissociation is possible on SrO-terminated surface which is in agreement with the available experimental data for SrTiO$_3$. Accordingly, the arrangement of H-bonds between the hydroxyl hydrogens and surface oxygens plays an important role in stabilizing the water adsorption on the metal oxide surfaces.
2. The water is adsorbed in the molecular form on all MO$_2$-terminated surfaces under consideration, whereas the water adsorption on SrO-terminated surface strongly depends on the nature of the transition metal. The energy of water dissociation on SrO surface of SrZrO$_3$ and SrHfO$_3$ is much greater than the corresponding molecular adsorption energy. Moreover, no stable structure for molecular adsorption was found in the case of low coverage on the zirconate and hafniate SrO surfaces indicating the more basic nature of SrO surfaces for zirconate and hafniate than that for titanate.
3. The results of the $ab\ initio$ calculations together with experimental data provide a base for the developing of the classical model potentials, which can reproduce properties of both bulk crystals and their bare and hydroxylated surfaces. Accounting the ion-polarization effects via the shell model [23] allows to avoid the problems associated with the charge transferability between the physically different systems- bulk crystals, bare and hydroxylated surfaces.
4. The molecular mechanics calculations using the extended surface unit cells give evidence for the possible surface transformation and reconstruction upon relaxation and hydroxylation of cubic

Figure 4. Molecular adsorption of the one water molecule on TiO$_2$-terminated surface of SrTiO$_3$: (a) $ab\ initio$ result; (b) molecular mechanic result with the adjusted potential parameters. See Figure 2 for the atoms tints.
perovskites. These effects are more prominent when the water molecules are adsorbed at the low surface coverage.

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