



## Review

*Ab initio* study of proton dynamics on perovskite oxide surfaces

Fuyuki Shimojo

*Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan*

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**Abstract**

First-principles studies of the proton dynamics in perovskite oxides and the water adsorption on various oxide surfaces are briefly reviewed. Recent progress in the study of the microscopic mechanism of the proton adsorption from perovskite oxide surfaces is also presented. It is shown that dopant ions on the surface and oxygen vacancies in the inside just below the surface play an important role for the proton adsorption, while oxygen vacancies on the surface are influential for the dissociative adsorption of water molecules.

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*Keywords:* Proton; Perovskite oxides; Surface; Pseudopotential; *Ab initio*; Density functional theory**Contents**

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**1. Introduction**

The importance of high temperature proton conducting oxide solids has been emphasized for a wide variety of electrochemical applications [1]. Recently, much progress has been made in applying proton conductors to fuel cells, hydrogen sensors, and so on [2,3], although there remain many technological issues to be solved. In most of the applications, the control of chemical reactions at electrodes is one of the most critical issues. It is, therefore, important to understand the microscopic mechanism of molecular reactions on the surface of oxides or near the interface between oxides and metals in connection with an efficient technological application. For this purpose, theoretical

studies based on first-principles calculations would be indispensable.

So far, the static and dynamic properties of protons, such as stable positions and diffusion pathways, in proton conducting oxides have been elaborately investigated and clarified by first-principles theoretical studies [4–18]. Also, the adsorption of molecules on the surfaces of various oxides has been studied from first-principles, and their microscopic processes have been discussed thoroughly [19–42]. However, the mechanism of proton migration into the inside of oxides from the surface or interfaces has not yet been elucidated. In this paper, we provide a brief review of the first-principles theoretical work relating to the proton dynamics in oxides, especially perovskite oxides. First, we present first-principles studies of the dynamic properties of protons in the perovskite oxides. We then

*E-mail address:* [shimojo@kumamoto-u.ac.jp](mailto:shimojo@kumamoto-u.ac.jp)

describe first-principles investigations of the dissociative adsorption of water molecules on perovskite oxide surfaces. Also, we discuss the absorption mechanism of protons from the surfaces.

## 2. Proton dynamics in perovskite oxides

Islam and coworkers [4–6] have applied a first-principles method for the first time to protons in perovskite oxide  $\text{LaAlO}_3$ . They tried to calculate the energy barrier to proton diffusion by *ab initio* Hartree–Fock calculations for a small cluster.

We have studied the stable positions of a proton in Sc-doped  $\text{SrTiO}_3$  by optimizing the geometry of atoms in a supercell based on first-principles pseudopotential calculations [7]. It was shown that, in stable atomic configurations, the position of the proton is between two neighboring O ions, and the proton is bound to one O ion. This is consistent with the results of neutron diffraction experiments [43]. The position of the proton, obtained by our calculations, is on the opposite side of Ti (Sc) with respect to a line connecting the adjacent two O ions due to the Coulomb repulsion between Ti (Sc) and the proton.

Morinaga and coworkers have calculated the local electronic structures around protons in  $\text{SrTiO}_3$  [8] and  $\text{SrZrO}_3$  [9] using an isolated cluster model with DV-X $\alpha$  molecular orbital method. They discussed the energy level structures, such as donor and acceptor levels, near the band gap in detail. Recently, they have studied the optimized geometries, formation energies of interstitial proton, and activation energies for proton transfer in In-doped  $\text{AZrO}_3$  (A = Ca, Sr, Ba) by first-principles pseudopotential calculations [10].

Since the theoretical studies described above are based on the static structure, detailed discussions on the proton dynamics are limited. To investigate the microscopic mechanism of proton diffusion, it is crucially important to take into account the effects of temperature.

We have applied *ab initio* molecular-dynamics (MD) simulations to protons in Sc-doped  $\text{SrTiO}_3$  [11–13] and Y-doped  $\text{SrCeO}_3$  [14] to consider the finite temperature effects. Our simulation confirmed that there are two types of diffusion paths; one is the diffusion around an O ion while retaining the O–H bond, and the other is the diffusion between two neighboring O ions while switching the O–H bond. It was shown that the proton forms an O–H bond with the neighboring O ion, and the frequency of the stretching vibration of the O–H bond depends on the position of the proton in these crystals. It was found that, in Sc-doped  $\text{SrTiO}_3$ , there is a tendency for electrons to localize around O ions near Sc ions, while the electron density between Ti and O ions is higher than that in the undoped crystal. The electrons localized around O ions near Sc ions make the hydrogen bond (O...H bond) stronger, which is responsible for the lower frequencies of the O–H stretching vibration for protons near the Sc ion.

This fact means that protons can diffuse between two neighboring O ions more easily when they are near the dopant Sc ions.

In Y-doped  $\text{SrCeO}_3$ , there are many positions for protons, and the frequency of the O–H stretching vibration is distributed over a wide range. The probable migration paths of protons in Y-doped  $\text{SrCeO}_3$  are basically the same as those in Sc-doped  $\text{SrTiO}_3$  described above. However, the arrangement of the octahedrons formed by six O ions is greatly affected by the presence of protons in Y-doped  $\text{SrCeO}_3$ , and proton migrations between the third or fourth neighboring O ions are possible, which are not observed in Sc-doped  $\text{SrTiO}_3$ . We have also investigated the effects of O vacancies on the diffusion pathways of protons [13].

Islam et al. [15] have carried out *ab initio* MD simulations for protons in  $\text{CaZrO}_3$  doped with Ga, Sc, and In. They confirmed that protons diffuse from one O ion to the next accompanied with the vibrational dynamics of the oxygen sublattice. It was shown that binding energies for hydroxyl-dopant pairs are compatible with proton trapping energies observed experimentally.

Wahnström and coworkers [16–18] have investigated the local proton dynamics in In-doped  $\text{BaZrO}_3$  based on first-principles calculations. They showed that the frequency of O–H stretching vibration depends on the local configurations around protons, and emphasized that oxygen vacancies and dopant ions affect the proton mobility.

Toward a further understanding of the proton dynamics one has to investigate the time evolution of bonding properties associated with protons, which have not yet been studied so far. For this purpose, we have utilized the population analysis by expanding the electronic wavefunctions in an atomic orbital basis set [44,45]. Based on this analysis, we obtained the overlap population  $O_{ij}$  between the  $i$ th and  $j$ th atoms and the partial density of states (DOS)  $D_{\text{H}}(E)$  associated with protons as a function of time.

Fig. 1 shows the time evolution of atomic configuration around a proton obtained by *ab initio* MD simulations for Sc-doped  $\text{SrTiO}_3$ . In this figure, the proton migration between O ions (from  $\text{O}_1$  to  $\text{O}_2$ ) is displayed. The time evolution of  $O_{ij}(t)$  and  $r_{ij}(t)$  between the two O ions and proton is shown in Fig. 2. At  $t = 0$  fs, the proton is bonded to  $\text{O}_1$  as shown in Fig. 1(a), and therefore  $O_{ij}(t)$  for H– $\text{O}_1$  has a large value  $\sim 0.4$ , while  $O_{ij}(t)$  for H– $\text{O}_2$  is almost zero. For  $0 < t < 70$  fs,  $r_{ij}(t)$  for H– $\text{O}_2$  decreases gradually with time  $t$ , and  $r_{ij}(t)$  for H– $\text{O}_1$  oscillates around about 1 Å, which means that the proton migrates to  $\text{O}_2$  while keeping the H– $\text{O}_1$  bond. Accompanied with this migration,  $O_{ij}(t)$  for H– $\text{O}_2$  increases. Note that  $O_{ij}(t)$  for H– $\text{O}_1$  and H– $\text{O}_2$  are comparable for about 50 fs between 70 and 120 fs, which clearly shows that the proton is partially bonded to both O ions during the migration between the two O ions with switching the O–H bonds. For  $t > 120$  fs, the proton leaves  $\text{O}_1$  while keeping the H– $\text{O}_2$  bond, as  $r_{ij}(t)$  for H– $\text{O}_1$  increases gradually with  $t$  and  $r_{ij}(t)$  for H– $\text{O}_2$  oscillates around 1 Å.

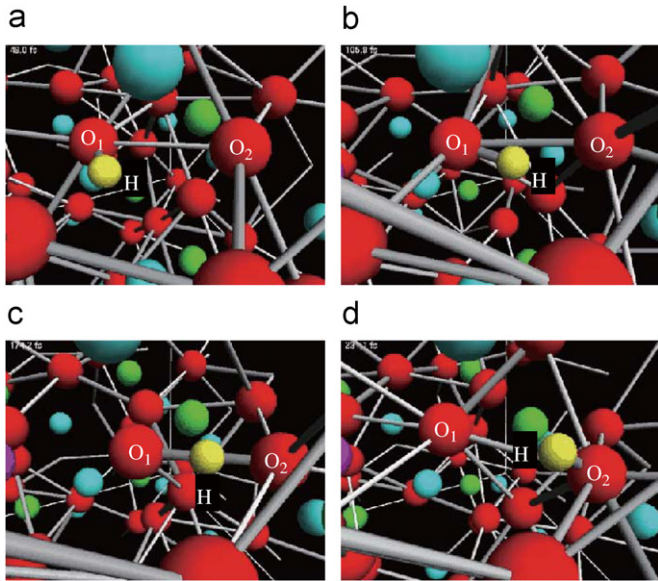


Fig. 1. Time evolution of atomic configuration around a proton obtained by *ab initio* MD simulations for Sc-doped SrTiO<sub>3</sub>. (a) 10 fs; (b) 50 fs; (c) 100 fs; (d) 170 fs.

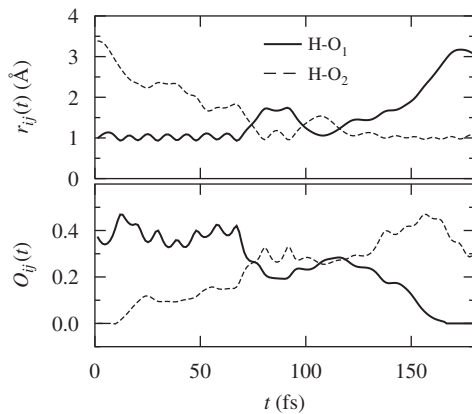


Fig. 2. Time evolution of interatomic distances  $r_{ij}(t)$  and overlap populations  $O_{ij}(t)$  between the two O ions and proton.

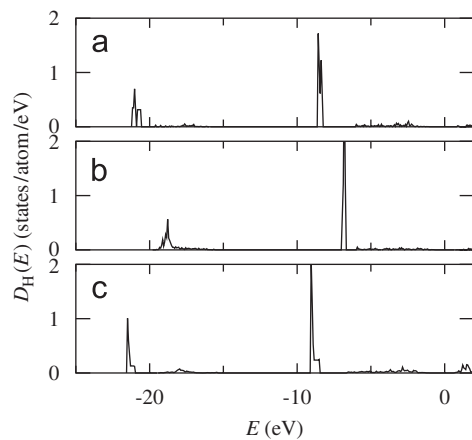


Fig. 3. Time evolution of partial electronic density of states  $D_H(E)$  associated with the proton. (a) 10 fs; (b) 100 fs; (c) 170 fs.

Fig. 3(a) shows the partial DOS  $D_H(E)$  associated with the proton at  $t = 10$  fs. The peaks at about  $E = -8$  and  $21$  eV correspond to the bonding states with  $2p$  and  $2s$  states of  $O_1$  ion, respectively. As displayed in Fig. 3(b) for  $t = 100$  fs, these peaks are kept during the migration between the two O ions, which confirms that the proton keeps the O–H (partial) bonds, although the energies are higher than those at  $t = 10$  fs. At  $t = 170$  fs, the proton is bonded only to  $O_2$ , and  $D_H(E)$  is similar to that at  $t = 10$  fs (see Figs. 3(a) and (c)).

### 3. Water molecule on perovskite oxide surfaces

In this section, we discuss the adsorption of water molecule on perovskite oxide surfaces. It has been known from experimental studies on the SrTiO<sub>3</sub> (1 0 0) surface [46] that no evidence for water dissociation is found on clean surfaces, which strongly suggests that water molecules dissociate at defect sites. It is, however, difficult to determine the structure of surfaces from experiments, and therefore theoretical investigations would be needed.

There exist several first-principles studies of the water adsorption on various oxide surfaces, whereas, to our knowledge, no first-principles investigations of the interaction between water molecules and perovskite oxide surfaces have been reported so far.

Among oxide surfaces, the water adsorption on the surface of TiO<sub>2</sub> has been most extensively studied by theoretical methods [19–24]. Beck et al. [23] have studied the adsorption of water molecules on the TiO<sub>2</sub> (0 1 1)-(2 × 1) surface by *ab initio* MD simulations combined with scanning tunneling spectroscopy experiments. They found that water molecules dissociate when the density of water molecules is low, while a mixed molecular/dissociated water monolayer is stabilized when the density of water molecules increases. They asserted that their observation basically obeys the rule proposed by Henderson [47] that the relative proximity between undercoordinated Ti and O ions on the surfaces is critical for the water dissociation. However, there is an argument against the rule. Lindan and Zhang [24] have shown by their first-principles calculations that water molecules dissociate on the TiO<sub>2</sub> (1 1 0) surface where the distance between surface Ti and O ions is fairly large. The detailed mechanism of the water adsorption on the TiO<sub>2</sub> surfaces is still an open question, whereas there is no argument that oxygen vacancies are active sites for the dissociation of water molecules.

The structure and energetics of water molecules adsorbed at the CeO<sub>2</sub> (1 1 1) surfaces have been studied by Kumar and Schelling [25] using the structural optimization technique based on first-principles calculations. They predicted that the contribution of the dipole–dipole interactions between adsorbed water molecules to the water adsorption energy for the clean surfaces becomes important as the coverage increases. It was found that water molecules are attracted more strongly to the surfaces, when oxygen vacancies exist near the surfaces.

Also, the dissociative and molecular adsorption of water molecules on the surfaces of various oxides, such as  $\text{Al}_2\text{O}_3$  [26,27],  $\text{SnO}_2$  [28–31],  $\text{SiO}_2$  [32–34],  $\text{V}_2\text{O}_5$  [35,36],  $\text{ZnO}$  [37–39], and  $\text{MgO}$  [40–42], has been studied by first-principles theoretical methods.

Here, we describe the results of *ab initio* MD simulations for water molecules on the surface of Sc-doped  $\text{SrTiO}_3$ , which were carried out to clarify the microscopic processes of the dissociative adsorption of water molecules on perovskite oxide surfaces.

Fig. 4 shows the time evolution of atomic configuration for the adsorption of a water molecule on the  $\text{TiO}_2$  (001) surface. At 0 fs, the water molecule is placed at a position 5 Å above the surface. Just below the molecule, an oxygen vacancy is introduced on the surface. Two Ti ions near the vacancy are replaced by Sc ions. As shown in Fig. 4, the water molecule dissociates, and the oxygen that initially forms the molecule occupies the position of the vacancy.

Fig. 5 shows the time evolution of the interatomic distances  $r_{ij}(t)$  and the overlap populations  $O_{ij}(t)$  between the protons ( $\text{H}_1$  and  $\text{H}_2$ ) and oxygen ( $\text{O}_1$ ) that initially form the water molecule. For  $t < 250$  fs, two  $r_{ij}(t)$  oscillate around 1 Å, and  $O_{ij}(t)$  have high values, which means that O–H bonds are formed within the molecule. At about 250 fs,  $r_{ij}(t)$  for  $\text{O}_1\text{--H}_1$  starts to increase, while the other keeps the initial distance. At the same time,  $O_{ij}(t)$  for  $\text{O}_1\text{--H}_1$  decreases quickly, which shows that the  $\text{O}_1\text{--H}_1$  bond is broken.

Fig. 6 shows the time evolution of  $r_{ij}(t)$  and  $O_{ij}(t)$  between Sc ions on the surface and the oxygen that initially forms the water molecule. It is found that  $O_{ij}(t)$  increase quickly at about 250 fs corresponding to the dissociation of the molecule. From these results, we see that the

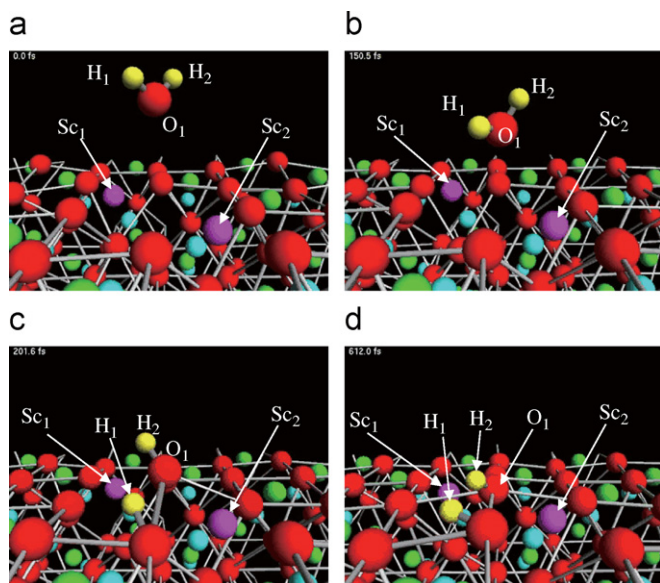


Fig. 4. Time evolution of atomic configuration for the adsorption of a water molecule on the  $\text{SrTiO}_3$  (001) surface with an oxygen vacancy. (a) 0 fs; (b) 200 fs; (c) 270 fs; (d) 800 fs.

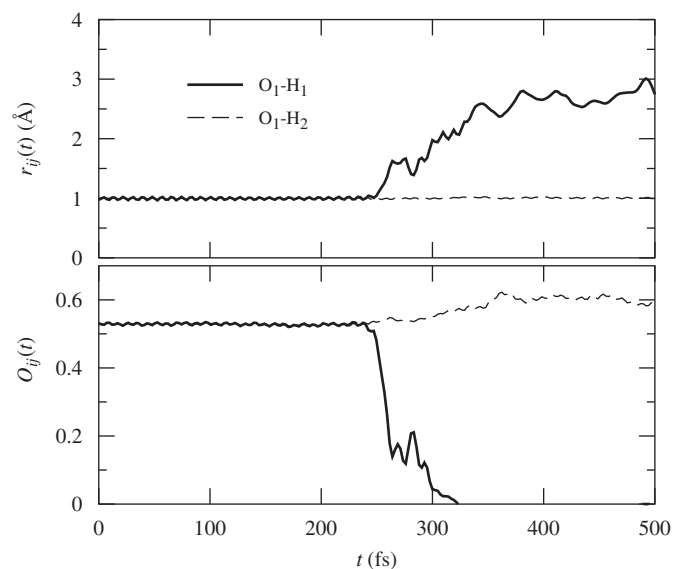


Fig. 5. Time evolution of interatomic distances  $r_{ij}(t)$  and overlap populations  $O_{ij}(t)$  between the protons and oxygen that initially form the water molecule.

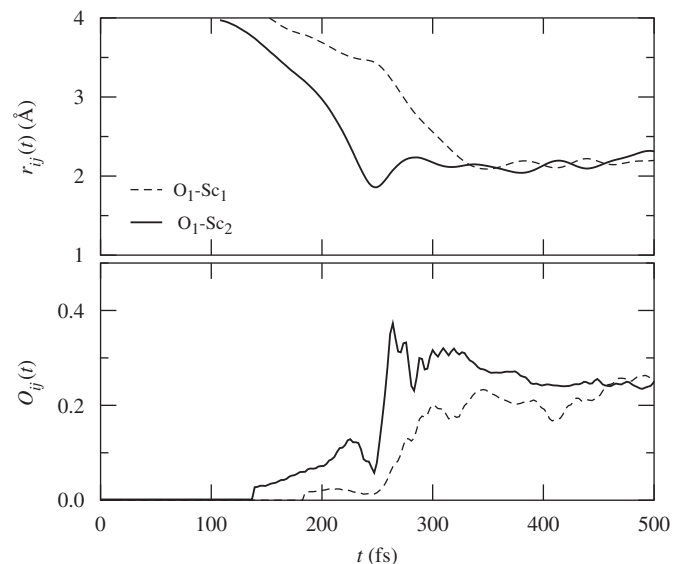


Fig. 6. Time evolution of interatomic distances  $r_{ij}(t)$  and overlap populations  $O_{ij}(t)$  between Sc ions on the surface and the oxygen that initially forms the water molecule.

dissociative chemisorption of water molecules on the perovskite oxide surfaces takes place with the bond switching between O–H and O–Sc (O–Ti) chemical bonds. Note that  $O_{ij}(t)$  for the  $\text{O}_1\text{--Sc}_2$  pair has finite values before the molecule dissociates.

#### 4. Proton dynamics on perovskite oxide surfaces

As described in the previous sections, the dynamic properties of protons in perovskite oxides have been

elucidated by first-principles theoretical methods. Also, the dissociative and molecular adsorption of water molecules on various oxide surfaces has been extensively studied by *ab initio* calculations. Especially, *ab initio* MD simulations have revealed the microscopic processes of the water adsorption on the perovskite oxide surfaces. In this section, we discuss the mechanism of the proton absorption from the surface of perovskite oxides.

Although the structural and vibrational properties of hydrogen on the surfaces of some oxides have been studied theoretically [48,49], the absorption mechanism of protons has not been well elucidated in an atomistic level so far.

First, we optimized the atomic geometries of two model systems for SrTiO<sub>3</sub> and SrCeO<sub>3</sub>, which have vacancy-free clean surfaces, by introducing a proton in various positions near the surfaces. Fig. 7 shows the total energies of the two systems as a function of the position of the proton. From this figure, it is found that the energy for the proton on the surface is lower than that for the proton in the interior, which means that protons prefer to stay on the surface rather than come into the inside near the clean surface. These results indicate that the presence of surface vacancies is important for the proton absorption. Note that the energy difference between the sites on the surface and in the interior in SrCeO<sub>3</sub> is smaller than that in SrTiO<sub>3</sub>, which indicates that the proton migrates to the inside of SrCeO<sub>3</sub> more easily compared with SrTiO<sub>3</sub> being in agreement with the experimental observations.

There are two major factors that determine the energy of a proton at each site. One is the energy gain by forming the hydrogen bond (O–H···O), and the other is the energy loss by the Coulomb repulsion between the proton and cations Ti<sup>4+</sup> or Ce<sup>4+</sup>. It is more advantageous to keep away from the cations on the surface than to form the hydrogen bond in the interior when the surface is clean. This is the reason why the proton has the lower energies on the clean surfaces.

Next, we carried out several computer simulations for a proton on the perovskite oxide surfaces to clarify the effects of (1) dopant ions on the surface, and (2) oxygen vacancies which exist in the interior just below the surface on the proton absorption.

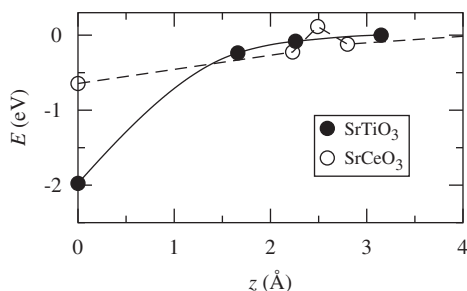


Fig. 7. Total energy as a function of the position of a proton.  $Z$  is the distance from the surface. The solid and open circles show the results for SrTiO<sub>3</sub> and SrCeO<sub>3</sub>, respectively.

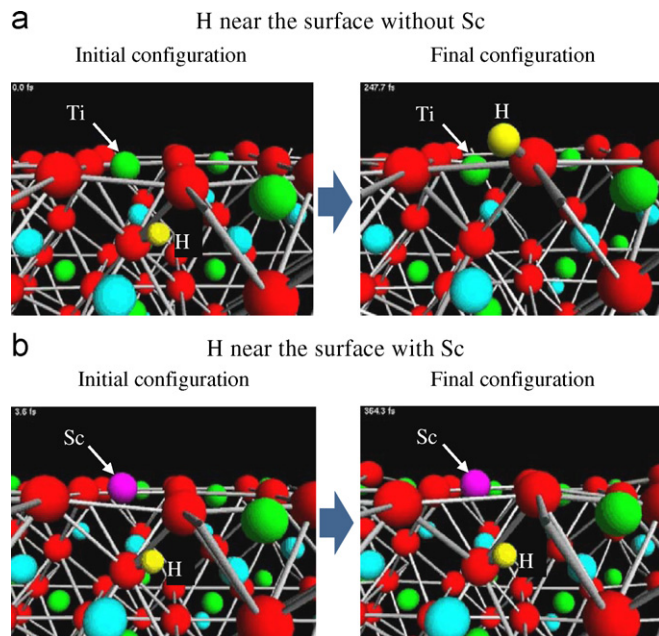


Fig. 8. Initial and final atomic configurations of *ab initio* MD simulations for SrTiO<sub>3</sub> (100) surfaces with a proton. In the initial configurations, the proton is bonded to an O ion just below (a) surface Ti and (b) surface Sc.

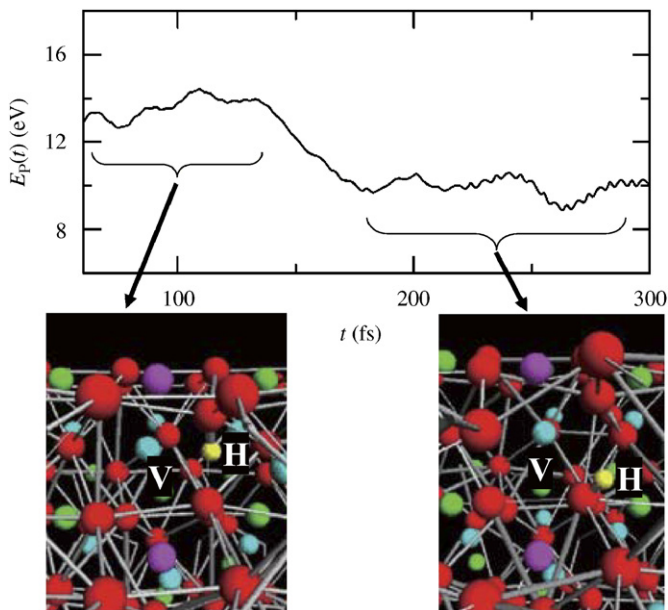


Fig. 9. Time evolution of the potential energy of a model system for SrCeO<sub>3</sub>. The proton stays near the surface for  $t < 130$  fs, and migrates into the inside between 130 and 180 fs. In the atomic configurations, 'V' denotes the position of an oxygen vacancy.

Fig. 8 shows the initial and final atomic configurations obtained by *ab initio* MD simulations for a proton introduced near the SrTiO<sub>3</sub> (100) surface. In the initial configurations, the proton is bonded to an oxygen ion just below the surface cation (Ti or Sc). It is found that the proton stays in the interior when there exists a dopant Sc

ion on the surface, while the proton migrates to the surface without Sc ions. It is considered that the energy loss by the Coulomb repulsion between the proton and  $\text{Sc}^{3+}$  is smaller than that between the proton and  $\text{Ti}^{4+}$ . Therefore, the proton stays in the inside below the surface Sc. Also, it has been known that electrons are more localized around O ions near Sc compared with O ions near Ti [13], which means that the energy gain by forming the hydrogen bond is larger when the proton exists near Sc. We conclude that these two effects of surface dopants play an important role in the proton absorption.

Fig. 9 shows the time evolution of the potential energy for a model system of  $\text{SrCeO}_3$  with a proton near the surface. An oxygen vacancy is introduced in the inside as denoted by 'V' in the figure. The proton stays near the surface oxygen before about 130 fs, and migrates to the inside for about 50 fs between 130 and 180 fs. It is found from the figure that the potential energy decreases accompanying this proton migration. These results clearly demonstrate that protons near the surface easily diffuse into the interior in  $\text{SrCeO}_3$  when there exist oxygen vacancies in the inside.

## 5. Conclusion

This paper presents a brief review of first-principles studies of the proton dynamics in perovskite oxides, and the water adsorption on various oxide surfaces. The dynamics properties of protons in perovskite oxides have been elucidated theoretically. The dissociative and molecular adsorption of water molecules on oxide surfaces has been extensively studied and well understood, although there are some arguments about the adsorption mechanism.

We have demonstrated that the population analysis is a powerful tool to study the microscopic mechanisms of proton diffusion in oxides and molecular reactions on surfaces.

We have discussed the dynamic properties of protons on perovskite oxide surfaces, and concluded that dopant ions on the surface and oxygen vacancies in the inside just below the surface play an important role for the proton absorption, while oxygen vacancies on the surface are influential for the dissociative adsorption of water molecules.

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