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## Adsorption, dissociation and diffusion behavior of $\text{H}_2\text{O}$ on the $\text{PuO}_2(111)$ surface from DFT + U-D3: the role of hydrogen bonding

 Huang Huang, Min Zhu, Fei Wu, Longxian Li and Yan Li \*

The interaction between  $\text{H}_2\text{O}$  and plutonium oxide is an essential aspect of researching plutonium corrosion. We systematically studied the adsorption, dissociation, and diffusion of  $\text{H}_2\text{O}$  molecules on the  $\text{PuO}_2(111)$  surface with the DFT + U-D3 scheme. We find that the top of the Pu atom is the most stable adsorption site for  $\text{H}_2\text{O}$  molecules on the  $\text{PuO}_2(111)$  surface. When multiple  $\text{H}_2\text{O}$  molecules are adsorbed, hydrogen bonding between molecules can increase the average adsorption energy.  $\text{H}_2\text{O}$  molecules will dissociate into H atoms and O-H groups under certain conditions. We have paid special attention to the role of hydrogen bonds between  $\text{H}_2\text{O}$  molecules. When the coverage of  $\text{H}_2\text{O}$  molecules is low, hydrogen bonds can significantly promote the adsorption and dissociation of  $\text{H}_2\text{O}$  molecules. And  $\text{H}_2\text{O}$  tends to exist on the surface of plutonium oxide in dissociated and molecular mixed states. The H atoms produced by the dissociation of  $\text{H}_2\text{O}$  molecules are not easily diffused, which may be related to the hydrogen bonding between O-H groups. This work has important theoretical significance for deepening the understanding of the corrosion mechanism of plutonium.

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## 1 Introduction

Plutonium will quickly form a complex oxide layer on the surface when exposed to air. In environments with high humidity, the corrosion process significantly changes, and the corrosion rate increases exponentially. It is significant to study the interaction between  $\text{H}_2\text{O}$  molecules and the surface of plutonium oxide to reveal this increasing effect.

Despite the significant difficulty in conducting experimental research on plutonium, pioneers have established a basic understanding of the interaction between  $\text{H}_2\text{O}$  molecules and plutonium oxides through unremitting efforts. Stackebake<sup>1</sup> research indicates that  $\text{H}_2\text{O}$  vapor undergoes desorption within two ranges of 100 °C to 150 °C and 300 °C to 350 °C, with a single physical adsorption process accompanied by two chemical adsorption processes. Several years later, Stackebake<sup>2</sup> conducted research on the characteristics of the reaction between binary plutonium oxide and  $\text{H}_2\text{O}$ , obtained a series of conclusions, and proposed corresponding mechanisms that are still unclear. The Stackebake team's Haschke<sup>3</sup> studied the strengthening effect of moisture on plutonium oxide corrosion. Their research showed that the corrosion rate is not significantly related to  $\text{H}_2\text{O}$  pressure above 200 °C or below -25 °C. In comparison, the correlation between the two is high, near 100 °C. In subsequent studies, Haschke<sup>4</sup> presented the adsorption process of plutonium oxide in  $\text{H}_2\text{O}$  at 25 °C and its humidity

dependence. They believed that  $\text{H}_2\text{O}$  is regulated through a series of different steps, including five types of adsorbate oxide interactions. In his research on plutonium oxides, Haschke<sup>5</sup> found that this non-stoichiometric oxide is formed through the reaction of carbon dioxide with  $\text{H}_2\text{O}$  and carbon dioxide with oxygen catalyzed by  $\text{H}_2\text{O}$ . Haschke<sup>6</sup> also found that the enhanced corrosion of plutonium oxide by  $\text{H}_2\text{O}$  is achieved through  $\text{H}_2\text{O}$  catalytic cycling. Farr's<sup>7</sup> research indicates that hydroxyl groups are commonly present on the surface of  $\text{PuO}_2$  exposed to  $\text{H}_2\text{O}$  vapor or ambient air, and the active sites for  $\text{H}_2\text{O}$  and other minor molecule reactions can be updated through thermal or radiation effects. Paffett<sup>8</sup> studied the thermodynamic interactions between  $\text{H}_2\text{O}$  and actinide oxide surfaces. This process was confirmed, and the estimated values were corrected. The adsorption energy values for the first layer dissociation adsorption and the second layer molecular adsorption at 371 K were reported to be -1.82 and -1.11 eV, respectively.

A more detailed mechanism study is conducted through theoretical calculations. Jomard<sup>9</sup> studied the adsorption and dissociation processes of  $\text{H}_2\text{O}$  molecules on the  $\text{PuO}_2(110)$  surface, which resulted in two hydroxyl groups asymmetrically placed on the surface, and the dissociation was thermally activated. At low temperatures, molecular states can exist in a metastable configuration for a long lifetime. This surface hydration does not affect the oxidation state of Pu atoms. The research results of Tegner *et al.*<sup>10</sup> on the adsorption of  $\text{H}_2\text{O}$  molecules on various surfaces of  $\text{PuO}_2$  and  $\text{UO}_2$  indicate that the mixture of molecules and dissociated  $\text{H}_2\text{O}$  adsorption is the



most stable on the  $\{111\}$  surface. On the other hand, fully dissociated  $\text{H}_2\text{O}$  adsorption is the most stable on the  $\{110\}$  and  $\{100\}$  surfaces, resulting in a completely hydroxylated monolayer. They also compared the adsorption of  $\text{H}_2\text{O}$  molecules on the surface of  $\text{PuO}_2$  with oxygen vacancy defects.<sup>11</sup> Results indicate that the vacancy creation substantially changes the most stable mode of  $\text{H}_2\text{O}$  adsorption on the  $\{111\}$  surface, such that a strong preference for dissociative adsorption on the substoichiometric surface replaces the almost degenerate molecular and dissociative adsorptions on the pristine surface. Tegner<sup>12</sup> also studied the adsorption of multilayer  $\text{H}_2\text{O}$  molecules on the surface of  $\text{PuO}_2$ . After several layers of adsorption, the adsorption energy gradually decreases and tends to stabilize. In this state, the adsorption mainly comes from hydrogen bonds between  $\text{H}_2\text{O}$  molecules. Wellington's<sup>13</sup> study on the adsorption of  $\text{H}_2\text{O}$  molecules on various surfaces of  $\text{PuO}_2$  shows that the energy of molecules and dissociative adsorption is similar on the  $\{111\}$  surface, while on the  $\{110\}$  surface, there is a clear tendency towards dissociative adsorption. Zhang Cui<sup>14</sup> analyzed the dissociation of  $\text{PuO}_2(110)$  surface and found that the dissociation of  $\text{H}_2\text{O}$  on the surface is a two-step hydroxylation process of monomers and clusters, with different mechanisms involved. For cluster  $\text{H}_2\text{O}$ , hydrogen bonding interactions between  $\text{H}_2\text{O}$  molecules promote dissociation and lead to a more stable dissociation state than individual molecules. Wang<sup>15</sup> studied the adsorption, diffusion, and dissociation processes of individual  $\text{H}_2\text{O}$  molecules on the surface of  $\alpha\text{-Pu}_2\text{O}_3(111)$ , and the results showed that  $\text{H}_2\text{O}$  molecules were preferentially adsorbed on surface oxygen vacancies with shallow adsorption energy. Wang's team<sup>16</sup> also analyzed the kinetic process of adsorption and dissociation of  $\text{H}_2\text{O}$  molecules on the surface of  $\text{Pu}_2\text{O}_3(111)$ , and confirmed the hydrogen bonding and hydrogen transfer reactions within clusters, which promoted the dissociation of  $\text{H}_2\text{O}$  molecules on the surface of  $\text{Pu}_2\text{O}_3(111)$ . The adsorbed  $\text{H}_2\text{O}$  tends to dissociate into hydrogen atoms and hydroxyl groups in addition to dissociating into hydrogen molecules and oxygen atoms. Zhang Le *et al.*<sup>17–20</sup> conducted a series of studies on the interaction between  $\text{H}_2\text{O}$  and plutonium oxides. They first analyzed the modulation mechanism of  $\text{H}_2\text{O}$  polarons adsorbed on the surface of  $\text{PuO}_2(111)$ , and found during the comparison with  $\text{CO}_2$  that electron polarons tend to promote  $\text{H}_2\text{O}$  adsorption, while hole polarons tend to promote  $\text{CO}_2$  adsorption. In addition, studies on the adsorption thermodynamics of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on  $\text{PuO}_2(111)$  surfaces have found that as coverage increases, the adsorption form of  $\text{H}_2\text{O}$  will change from a molecular state to a mixed adsorption state, but  $\text{CO}_2$  always adsorbs in a molecular state. The difference in adsorption behavior is mainly due to the hydrogen bonding and Coulomb interaction between the adsorbed molecules. They also believe that the two different O coordination numbers of Pu on the surface of  $\text{Pu}_2\text{O}_3(111)$  play a crucial role in the selective adsorption of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on the surface sites. In recent work, they focused on the hydroxyl group promoting  $\text{H}_2$  release reaction after the decomposition of  $\text{H}_2\text{O}$  on the surface of Pu oxide and found that both  ${}^2\text{H}$  and  ${}^2\text{OH}$  can promote the  $\text{H}_2$  release process, especially when the surface of  $\text{PuO}_2$  is reduced to  $\text{Pu}_2\text{O}_3$ , but the reaction mechanisms of the

two are different. In the above theoretical research, people have focused on the adsorption configuration and energy issues between the surface of plutonium oxide and  $\text{H}_2\text{O}$  molecules, as well as the effects of dissociation and O atom vacancy defects. However, a complete understanding of the adsorption dissociation and diffusion processes is still unclear. The understanding of the impact of hydrogen bonding between  $\text{H}_2\text{O}$  molecules on adsorption, dissociation, and subsequent diffusion is still relatively vague.

In this work, a first principles approach based on DFT +  $U$ -D3 was used to systematically investigate the adsorption, dissociation, and diffusion processes of  $\text{H}_2\text{O}$  molecules on the surface of  $\text{PuO}_2(111)$ . The rest of this paper is organized as follows. The details of the computational method are described in Section 2, and the results are discussed in Section 3. Section 4 contains the main conclusions.

## 2 Methods and computational details

The first-principles calculations were performed by the Vienna *ab initio* simulation package (VASP).<sup>21</sup> The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) is used for the exchange–correlation interaction of electrons.<sup>22,23</sup> The Hubbard model is used within the DFT +  $U$  method in the Dudarev formalism to treat strong on-site Coulomb interaction.<sup>24</sup> An effective  $U$  ( $U_{\text{eff}} = U - J$ ; *i.e.*, the difference between the Coulomb  $U$  and exchange  $J$  parameters, hereafter referred to as  $U$ ) value of 4 eV is selected for the 5f electrons of Pu and U, according to our previous calculations<sup>25,26</sup> and other computational experience.<sup>10,12,14,18,20,27–29</sup> We use the widely accepted collinear 1-k antiferromagnetic (AFM) states along the  $\{111\}$  orientations for the magnetic orders.<sup>30,31</sup> The Brillouin zone was sampled with a  $3 \times 3 \times 1$   $k$ -points mesh for the surface models generated by the Monkhorst–Pack method.<sup>32</sup> The cutoff energy is set to 520 eV. When optimizing the structure, the conjugate gradient method is used to search for the minimum energy value, the energy convergence is interpreted as  $1 \times 10^5$  eV, and the force convergence criterion is set to  $0.01 \text{ eV \AA}^{-1}$ . The van der Waals correction is described by the DFT-D3 method.<sup>33,34</sup>

$\text{PuO}_2$  crystallizes in the cubic fluorite (spacegroup:  $Fm\bar{3}m$ ) structures with lattice parameters of 5.396 Å. Our calculated result is 5.432 Å, with an error of 6.6% in the experiment, which is within an acceptable range. We adopted a  $\text{PuO}_2(111)$  surface slab model (shown in Fig. 1), consisting of five layers of plutonium atoms with 20 Pu atoms and 40 O atoms and a vacuum spacing of 20 Å, to avoid the interaction between periodic images. In the calculation of adsorption, the plutonium atoms in the top two layers (including nearby oxygen atoms) are allowed to relax together with the adsorbate, while the atoms in the other layers are frozen at optimized volume positions.

The adsorption energy ( $E_a$ ) of molecules on the surface is expressed as

$$E_a = E_{\text{slab+P}} - E_{\text{slab}} - E_{\text{P}}$$

where  $E_{\text{slab+P}}$  shows the total energy of the adsorption system,  $E_{\text{slab}}$  means the total energy of slab.  $E_{\text{P}}$  means the total energy of



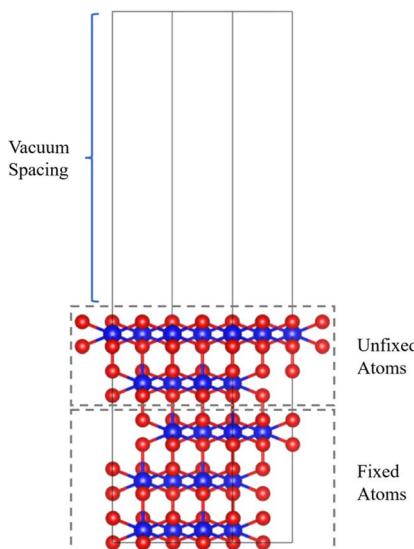


Fig. 1  $\text{PuO}_2(111)$  surface model diagram. Red spheres are oxygen atoms, and blue spheres are plutonium atoms.

the free particle. For the simultaneous adsorption of multiple particles of the same type, the average adsorption energy ( $E_{\text{a-ave}}$ ) must be considered. The average adsorption energy is expressed as

$$E_{\text{a-ave}} = (E_{\text{slab+P}} - E_{\text{slab}} - nE_{\text{P}})/n$$

A negative of  $E_{\text{a}}$  means heat release and spontaneous, and *vice versa*.

The  $\text{H}_2\text{O}$  dissociation on  $\text{PuO}_2(111)$  surfaces was explored using a climbing-image nudged elastic band (CI-NEB). The geometries of intermediate states and the activation energy were obtained *via* the simultaneous energy minimization of these discretized images between known initial and final states. In these CI-NEB calculations, relatively low accuracy is acceptable. The energy convergence is interpreted as  $5 \times 10^4$  eV, and the force convergence criterion is set to  $0.02 \text{ eV } \text{\AA}^{-1}$ .

### 3 Results and discussion

#### 3.1 Adsorption geometries and energetics of a single $\text{H}_2\text{O}$ molecule

After analysis, we found three adsorption sites for  $\text{H}_2\text{O}$  molecules on the surface of  $\text{PuO}_2(111)$ : the Pu atomic top site, Pu atomic bridge site, and Pu atomic hole site (Fig. 2).  $\text{H}_2\text{O}$  molecules can approach adsorption sites in three different postures: the molecule plane is parallel to the  $\text{PuO}_2(111)$  surface (abbreviated as P), the molecule plane is vertical to the  $\text{PuO}_2(111)$  surface with the H-H axis parallel to the  $\text{PuO}_2(111)$  surface (abbreviated as V1), and the molecule plane is vertical to the  $\text{PuO}_2(111)$  surface with the H-H axis vertical to the  $\text{PuO}_2(111)$  surface (abbreviated as V2), as shown in Fig. 3.

In a cubic box with side lengths of  $10 \text{ \AA}$ , the free  $\text{H}_2\text{O}$  molecule was simulated. The optimized O-H bond length and

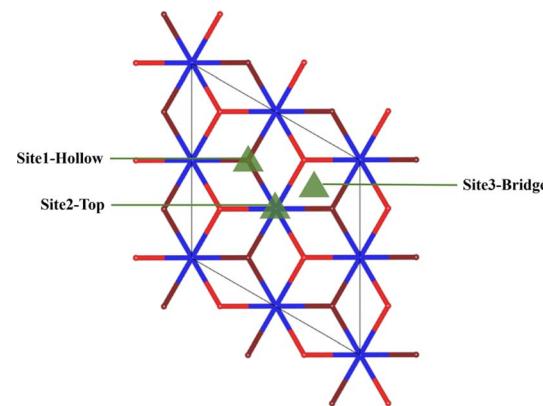


Fig. 2 Schematic diagram of adsorption points. Red spheres are the surface oxygen atoms, brown spheres are the secondary subsurface oxygen atoms, and blue spheres are plutonium atoms.

bond angle ( $\angle \text{H-O-H}$ ) are  $0.97 \text{ \AA}$  and  $104^\circ$ , which is very close to the experimental values of  $0.96 \text{ \AA}$  and  $104.45^\circ$ .

H-V1 represents  $\text{H}_2\text{O}$  molecules approaching the surface at the hollow site in a V1 posture. The optimized adsorption energy for configurations is shown in Table 1.

From the perspective of adsorption configuration, when the H-H axis of  $\text{H}_2\text{O}$  molecules is parallel to the surface, regardless of the initial placement point, the optimized solution can always be at the top position of the surface Pu atom, and the  $\text{H}_2\text{O}$  molecule plane is parallel to the surface. In the adsorption configuration,  $\text{H}_2\text{O}$  molecules move slightly in the direction indicated by the two H atoms. The O-H bond is slightly elongated, which means  $\text{H}_2\text{O}$  molecules tend to dissociate. The above situation is mainly due to the interaction between

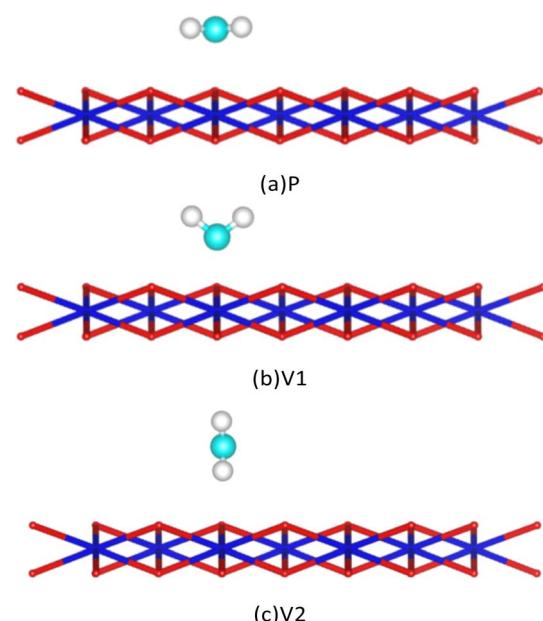


Fig. 3 Schematic diagram of the posture of  $\text{H}_2\text{O}$  molecules approaching the surface. Cyan spheres are oxygen atoms of  $\text{H}_2\text{O}$ , and white spheres are hydrogen atoms of  $\text{H}_2\text{O}$ .



Table 1 The adsorption energy of  $\text{H}_2\text{O}$  molecules with different configurations on the surface

| Configuration          | H-P    | H-V1   | H-V2   | T-P    | T-V1   | T-V2   | B-P    | B-V1   | B-V2   |
|------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Adsorption energy (eV) | -0.756 | -0.743 | -0.431 | -0.781 | -0.773 | -0.521 | -0.775 | -0.765 | -0.321 |

plutonium oxide and  $\text{H}_2\text{O}$ , where the H atom in  $\text{H}_2\text{O}$  molecules tends to interact with the O atom. In contrast, the O atom in  $\text{H}_2\text{O}$  tends to interact with the Pu atom. Under these two interactions,  $\text{H}_2\text{O}$  molecules will adsorb on the  $\text{PuO}_2(111)$  surface in a relatively fixed posture and undergo strong interactions on the surface, resulting in higher adsorption energy. When the H-H axis of the  $\text{H}_2\text{O}$  molecule is perpendicular to the surface, the H atom closest to the surface plays the leading role, while the O atom and another H atom are relatively far from the surface and cannot interact strongly with the surface atoms, resulting in smaller adsorption energy and different adsorption configurations.

### 3.2 Dissociation of a single $\text{H}_2\text{O}$ molecule

The CINEB method was used to explore the dissociation process of  $\text{H}_2\text{O}$  molecules. This method has played an important role in surface research related to plutonium multiple times. The CINEB method requires determining a stable and reasonable initial state (IS) and final state (FS).

In the initial state before dissociation,  $\text{H}_2\text{O}$  stably adsorbs on the surface in molecular form. Based on the analysis of the adsorption of  $\text{H}_2\text{O}$  molecules at various points on the Pu surface, we selected T-P as the IS. Compared to IS, the setting of FS needs to be carefully considered. Theoretical studies have shown that an  $\text{H}_2\text{O}$  molecule adsorbed on the surface of plutonium oxide may dissociate into an H atom and an OH group under the influence of external energy. In previous research, we also found the dissociation trend of  $\text{H}_2\text{O}$  molecules. For the H atom, the stable adsorption point is at the top position of the surface O atom, which has been validated in our previous work.<sup>35</sup> We also conducted an adsorption analysis similar to  $\text{H}_2\text{O}$  molecules for the OH group. The adsorption energy of each point is shown in Table 2. In terms of energy, the most stable adsorption site for OH is at the top of the Pu atom. After the dissociation of  $\text{H}_2\text{O}$  molecules into H atoms and OH groups, the two types of particles will exist on their respective most stable sites on the surface of  $\text{PuO}_2$ , forming the dissociation adsorption state of  $\text{H}_2\text{O}$  molecules. After sufficient relaxation, the desired FS is obtained.

Fig. 4 shows the various steps of dissociation of a single  $\text{H}_2\text{O}$  molecule on the surface of  $\text{PuO}_2(111)$ . The energy of the entire system increases from the IS to TS1, during which the O-H bonds of  $\text{H}_2\text{O}$  molecules are stretched after the system absorbs

energy. From TS1 to TS2, the energy continues to rise, requiring further absorption of energy to cross the energy barrier of 0.831 eV and achieve the breaking of O-H bonds. After crossing the energy barrier, the system energy gradually decreases until the H atom detached from the  $\text{H}_2\text{O}$  molecule combines with the O atom on the surface of  $\text{PuO}_2$  to form a structure, and the O-H group of the  $\text{H}_2\text{O}$  molecule combines with the Pu atom on the surface of  $\text{PuO}_2$ .

### 3.3 Adsorption of multiple $\text{H}_2\text{O}$ molecule

There are hydrogen bonds (HBs) between  $\text{H}_2\text{O}$  molecules within a specific range, and this special intermolecular force can have a particular impact on the adsorption process, resulting in apparent differences when individual  $\text{H}_2\text{O}$  molecules and  $\text{H}_2\text{O}$  molecule clusters interact with the surface of Pu oxide. To analyze this differences, multiple  $\text{H}_2\text{O}$  molecule cluster adsorption models with different coverage were constructed based on the stable adsorption sites of a single  $\text{H}_2\text{O}$  molecule (Fig. 5). There is a mutual correspondence between the O atom in  $\text{H}_2\text{O}$  molecules and the Pu atom on the surface. Given this, we define coverage as the proportion of  $\text{H}_2\text{O}$  molecules covering the top positions of surface Pu atoms.

The average adsorption energy of each molecule and bond length of O-H are shown in Table 3. When multiple  $\text{H}_2\text{O}$  molecules exist on the surface of Pu, the average adsorption energy is higher than that of a single  $\text{H}_2\text{O}$  molecule, that is, the interaction between  $\text{H}_2\text{O}$  molecules and the surface is strengthened. As the coverage increases, the average adsorption energy of each  $\text{H}_2\text{O}$  molecule on the surface first increases and then decreases. The result is consistent with Tegner's.<sup>10</sup> The

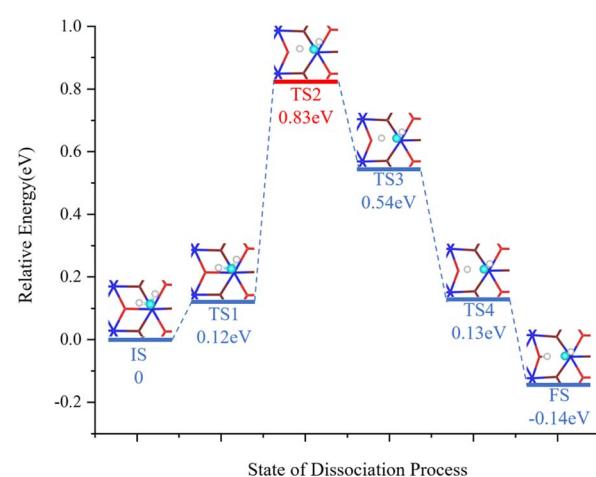
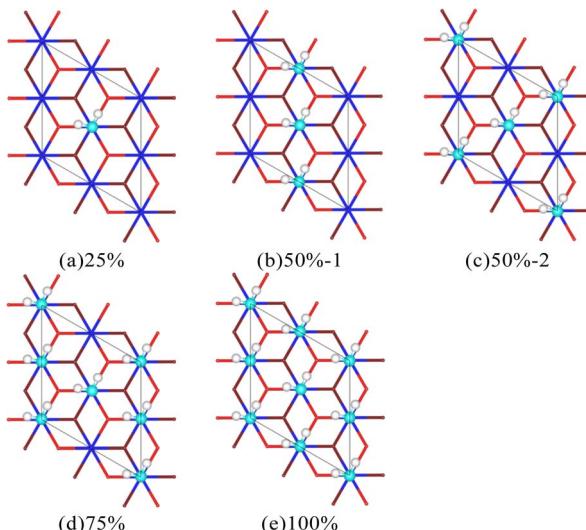


Fig. 4 The minimum-energy path for  $\text{H}_2\text{O}$  dissociation. The CINEB simulation consists of 6 images. Zero-point energy corrections are not included.

Table 2 The adsorption energy of O-H group with different configurations on the surface

| Configuration          | Hollow | Top    | Bridge |
|------------------------|--------|--------|--------|
| Adsorption energy (eV) | -0.311 | -1.243 | -0.531 |

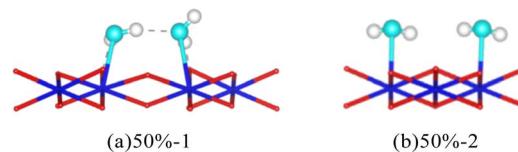


Fig. 5 Multiple  $\text{H}_2\text{O}$  molecules adsorption configurations.

increase in O-H bond length indicates a decrease in bond strength, indicating a more pronounced trend of bond breakage. Interestingly, with a coverage rate of 50%, different arrangements can also lead to differences in the adsorption energy of  $\text{H}_2\text{O}$  molecules on the surface. The process of interaction between  $\text{H}_2\text{O}$  molecules and the  $\text{PuO}_2(111)$  surface can cause the plane of  $\text{H}_2\text{O}$  molecules to no longer be parallel to the surface, as shown in Fig. 6. After relaxation, the distance between the donor and acceptor of hydrogen bonds in the 50%-1 system is 2.95 Å, while the distance between the two in the 50%-2 system is 3.19 Å. When  $\text{H}_2\text{O}$  molecules are vertically arranged on the surface, the strong hydrogen bonding between molecules significantly promotes the adsorption of  $\text{H}_2\text{O}$  molecules. When  $\text{H}_2\text{O}$  molecules are horizontally arranged, the hydrogen bonding between molecules is weak, and the promoting effect on adsorption is not significant.

In addition, the O-H bond length also exhibits some variation characteristics. Therefore, it is worth further attention to how the dissociation process changes when multiple  $\text{H}_2\text{O}$  molecules exist on the surface. We conducted a series of  $\text{H}_2\text{O}$  molecule dissociation analyses using the CINEB method.

$\text{H}_2\text{O}$  adsorption in fully molecular (abbreviation as M), fully dissociative (abbreviation as D), mixed molecular, and dissociative (abbreviation as M-D) states on  $\text{PuO}_2(111)$  surface, respectively. In our periodic model of the surface of  $\text{PuO}_2(111)$ , there are a total of four Pu atoms, corresponding to four  $\text{H}_2\text{O}$  molecules with 100% coverage. The adsorption energies corresponding to each dissociation process are shown in Table 4. It can be observed that the decomposition of one of the two  $\text{H}_2\text{O}$

Fig. 6 The configuration of  $\text{H}_2\text{O}$  molecules arranged horizontally and vertically after relaxation.

molecules occurs very easily, and it does not require external energy input. As a comparison, if both molecules dissociate, it requires some external energy input. For the case of four  $\text{H}_2\text{O}$  molecules with a coverage rate of 100%, when all three  $\text{H}_2\text{O}$  molecules are in a dissociation state, the energy required for the dissociation of the last molecule is even higher than that of a single  $\text{H}_2\text{O}$  molecule. In summary, when surface  $\text{H}_2\text{O}$  molecules are not saturated, intermolecular hydrogen bonds can promote dissociation. When water molecules are saturated, the effect of hydrogen bonds cannot compensate for the energy loss caused by the mismatch in the number of oxygen ( $\text{PuO}_2$ ) and hydrogen ( $\text{H}_2\text{O}$  atoms). The previous dissociation is prone to occur, while the energy required for subsequent dissociation gradually increases. The coexistence of hydroxyl groups and  $\text{H}_2\text{O}$  molecules on the surface of plutonium oxide was also observed in the experiment.<sup>36</sup>

### 3.4 H atomic diffusion

For the hydrogenation corrosion of metals, hydrogen adsorbed in an atomic state on the surface may subsequently diffuse internally under certain conditions. In this section, we first analyze the diffusion of a single hydrogen atom adsorbed on the surface O atom of the  $\text{PuO}_2(111)$  surface. Two diffusion paths were established, with diffusion path 1 being H atom diffusing from the top position of the surface oxygen atom (OT1) to the top position of the adjacent surface oxygen atom (OT2), and diffusion path 2 being H atom diffusing from the top position of the surface oxygen atom (OT1) to the top position of the adjacent subsurface oxygen atom (SOT1), as shown in Fig. 7. The energy barrier that diffusion path 1 needs to cross is 1.4 eV, and the energy barrier that diffusion path 2 needs to cross is 2.3 eV. From an energy perspective, H atoms tend to exist more on the surface of  $\text{PuO}_2(111)$ , indicating that the surface of  $\text{PuO}_2(111)$  can act as a hydrogen barrier, which is consistent with Yu's<sup>37</sup> judgment on  $\text{PuO}_2(110)$ .

Subsequently, we analyzed the diffusion of hydrogen atoms adsorbed on the surface of  $\text{PuO}_2(111)$  in the dissociated state of a single  $\text{H}_2\text{O}$  molecule. Three diffusion paths were also established. To distinguish them, define them as paths 3, 4, and 5, as shown in Fig. 8. The diffusion energy barriers of the three paths

Table 3 The adsorption energy and the bond length of O-H group with different configurations on the surface

| Coverage                         | 25%    | 50%-1  | 50%-2  | 75%    | 100%   |
|----------------------------------|--------|--------|--------|--------|--------|
| Adsorption energy/molecules (eV) | -0.781 | -0.814 | -0.793 | -0.801 | -0.791 |
| The bond length of O-H (Å)       | 0.988  | 1.049  | 0.991  | 0.998  | 0.989  |



Table 4 The energy barrier of each dissociation process

|                     |             |           |           |             |
|---------------------|-------------|-----------|-----------|-------------|
| State change        | 1M → 1D     | 2M → 1M1D | 1D1M → 2D | 3M → 2M1D   |
| Energy barrier (eV) | 0.831       | 0         | 0.343     | 0.103       |
| State change        | 2M1D → 1M2D | 1M2D → 3D | 4M → 3M1D | 3M1D → 2M2D |
| Energy barrier (eV) | 0.331       | 0.513     | 0.111     | 0.367       |
| State change        | 2M2D → 1M3D | 1M3D → 4D |           |             |
| Energy barrier (eV) | 0.567       | 0.841     |           |             |

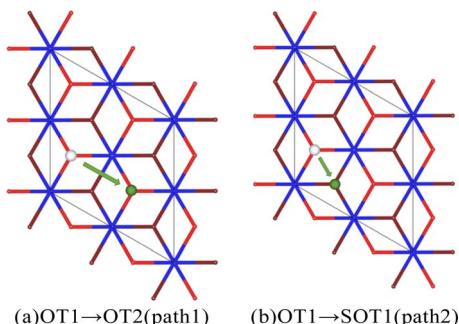
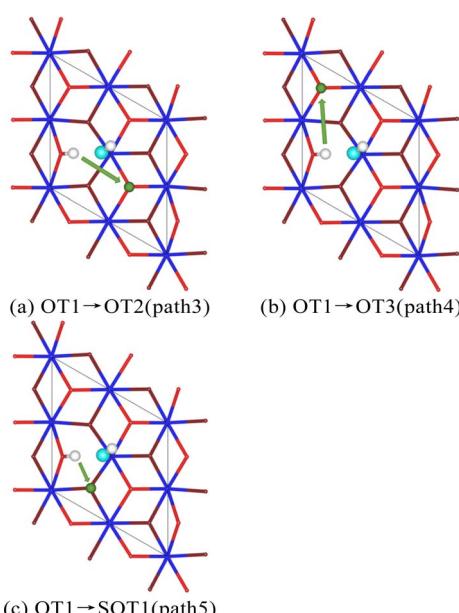


Fig. 7 The diffusion path of the single H atom.

Fig. 8 The diffusion path of the H atom from dissociation of  $\text{H}_2\text{O}$  molecule.

are 2.3, 3.1, and 4.3 eV, respectively. This indicates that whether diffusing to adjacent atoms on the surface or internally, the hydrogen atoms obtained from the dissociation of  $\text{H}_2\text{O}$  molecules require more stringent conditions than individual hydrogen atoms. We speculate that this may be related to the hydrogen bonds formed between hydroxyl groups. The first hydroxyl group is composed of a hydrogen atom dissociated from a  $\text{H}_2\text{O}$  molecule and a surface oxygen atom. The second hydroxyl group originates from the dissociation of a  $\text{H}_2\text{O}$  molecule.

## 4 Conclusions

We have performed a series of first-principles calculations with DFT +  $U$ -D3 of  $\text{H}_2\text{O}$  molecules on the  $\text{PuO}_2(111)$  surface to investigate the mechanism of  $\text{H}_2\text{O}$  adsorption, dissociation, and diffusion. The results indicate that hydrogen bonding has an impact on the surface behavior of  $\text{H}_2\text{O}$ . The conclusions are as follow:

(1)  $\text{H}_2\text{O}$  molecules will adsorb at the top of Pu atoms on the surface of  $\text{PuO}_2(111)$  in a fixed posture. Under certain external energy inputs,  $\text{H}_2\text{O}$  molecules will detach a proton to produce O-H groups that combine with surface Pu atoms. The removed proton will then combine with surface O atoms to form new O-H groups.

(2) When  $\text{H}_2\text{O}$  molecules do not fully cover the surface, hydrogen bonds between molecules can also promote the dissociation of  $\text{H}_2\text{O}$  molecules. When  $\text{H}_2\text{O}$  molecules cover the surface, the energy required for molecular dissociation gradually increases until the dissociation energy of the last molecule is equivalent to that of a single molecule.

(3) The H atom obtained from the dissociation of  $\text{H}_2\text{O}$  molecules requires more energy for diffusion than a single H atom. Diffusion inward is particularly difficult. We speculate that this is related to the hydrogen bonding between the O-H groups formed after dissociation.

## Conflicts of interest

There are no conflicts to declare.

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