

# *AIMD Study of Oxygen and Water on UO<sub>2</sub> Surface*

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**Abstract:** The first-principles molecular dynamics method was used to study the adsorption and dissociation of O<sub>2</sub> molecules and H<sub>2</sub>O molecules on the UO<sub>2</sub>(110) surface, and the adsorption and dissociation at different positions were compared and analyzed. For the case of dissociative adsorption, the radial distribution function is analyzed, and the bonding of U-O bonds is studied.

## 1. Introduction

Uranium metal is a nuclear material with excellent performance and has important applications in the fields of nuclear energy and national defense. During long-term storage, uranium components are prone to corrosion, causing material aging. The internal corrosion of uranium components will damage the structure of uranium, affect its mechanical properties, and reduce its reliability in high-temperature and high-pressure environments. The corrosion of the surface of uranium components will produce oxidized powder on the surface, and severely will form oxidation corrosion pits and destroy the surface structure of uranium components. Therefore, in application fields that require high surface geometry, surface corrosion may severely affect the performance of uranium components. In addition, if the oxide powder on the surface is disturbed by external forces and suspended in the air, radioactive dust will be formed, causing environmental pollution and harm to the health of related personnel.

An important oxide of uranium dioxide (UO<sub>2</sub>) is an important nuclear material in the field of nuclear energy and nuclear industry. Because of its excellent characteristics such as high radiation stability, high phase stability and high melting point, it has become widely used in today's fission nuclear reactors. One of the nuclear materials. In the storage environment, the surface of UO<sub>2</sub> inevitably comes into contact with H<sub>2</sub>O and O<sub>2</sub>, undergoes a chemical reaction, and is finally oxidized to U<sub>3</sub>O<sub>8</sub>. The phase transition process is accompanied by obvious changes in its physical properties, for example, its volume will expand by 35% [1]. Due to the expansion effect, the UO<sub>2</sub> film formed by oxidation on the surface of the uranium metal will generate stress, causing the UO<sub>2</sub> film to rupture and fall off, and lose its protective effect on the unoxidized uranium metal inside, causing the uranium metal to corrode continuously to the inside. In addition, the interaction of UO<sub>2</sub> and H<sub>2</sub>O will produce hazardous gas H<sub>2</sub>, which brings safety problems to storage [2-3]

Due to the complexity of the corrosion process of UO<sub>2</sub>, coupled with the limitations of experimental methods, existing research results cannot reveal its complete corrosion process. UO<sub>2</sub> surface corrosion is the initial stage of the complete corrosion process, and studying this process is of

great significance for understanding the corrosion behavior of  $\text{UO}_2$ . In this paper, first-principles molecular dynamics method is used to study the microscopic mechanism of  $\text{UO}_2$  surface corrosion. The expected research results will help to understand the microscopic mechanism of surface corrosion of  $\text{UO}_2$ , an important nuclear material, lay a foundation for the study of mesoscopic and macro-scale corrosion mechanism, and provide theoretical support for the research of its surface corrosion resistance technology. The rest of this article is organized as follows. Section 2 introduces the calculation methods and models, Section 3 discusses the calculation results, and Section 4 summarizes the main conclusions.

## 2. Methods and Models

### 2.1 Calculation method

The AIMD calculation in this article is carried out using the cp2k software package, using the DFT method of mixing Gaussian and plane wave basis sets GPW and GAPW, and the initial temperature is set to 300K. In classic MD calculations, the NPT ensemble is often used, but the number of atoms calculated by AIMD is limited, which will cause very severe pressure fluctuations and it is not easy to control the pressure, so the NVT ensemble is used. In order to speed up the calculation, the H atoms in  $\text{H}_2\text{O}$  are replaced with D atoms, and the time step is set to 1fs. U is a lanthanide element and there are 6d and 5f electrons. Both of these electrons are strongly correlated electrons. The traditional DFT method cannot accurately describe the gap. LDA and GGA ignore the strong correlation effect of electrons, so the correction effect is introduced and DFT+ is used. U method, take  $U-J=4.5\text{ev}$ . In the SCF iterative convergence, the OT method is selected, the convergence accuracy is  $1\text{E-}05$ , and the Brillouin zone integration uses the  $\Gamma$  point approximation. In the selection of the potential function, the 2s, 2p electrons of the O atom are used as the valence electrons, the 6s, 6p, 6d, 7s, and 5f electrons of the U atom are used as the valence electrons, and the remaining atoms use Geodecker-Teter-Hutter developed by LU[4] (GTH) Pseudopotential simulation.

### 2.2 Surface model

$\text{UO}_2$  is a face-centered cubic crystal, the space group code is  $225\text{-Fm}3\text{m}$ , the U atom is located at (0, 0, 0), the O atom is located at (0.25, 0.25, 0.25), and the lattice constant is  $5.468 \text{ \AA}$ [5].

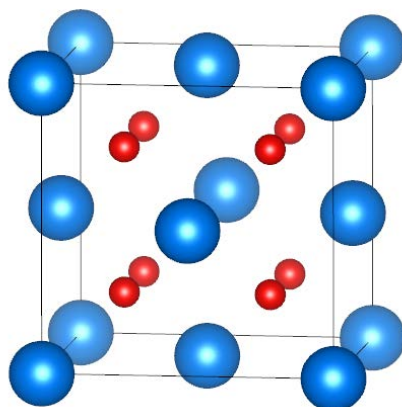


Figure 1:  $\text{UO}_2$  unit cell

In order to study the reaction process of  $\text{H}_2\text{O}$  and  $\text{O}_2$  molecules on the  $\text{UO}_2$  (110) plane, we constructed a slab model of  $p(2\times 1)$   $\alpha\text{-U}(110)$  crystal plane with 6 layers of atoms. There are 24 in a

single slab unit cell. U atoms, 64 O atoms. In the calculation, the bottom three layers of atoms were fixed, two layers of O atoms and one layer of U atoms, and the top three layers were released. Adsorption tends to occur in highly symmetrical positions, so we conducted studies on the bridge site, the top site, and the hollow site separately.

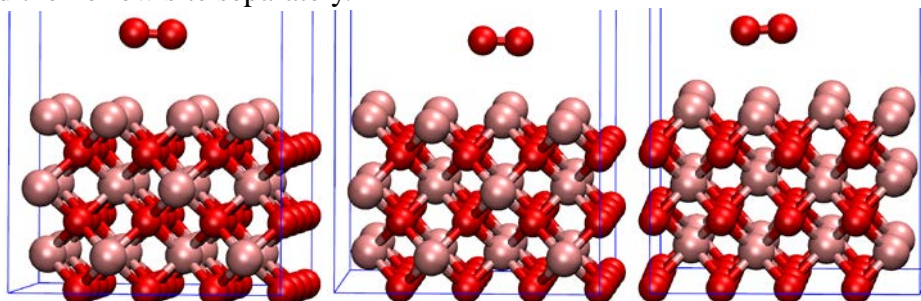


Figure 2: Three spatial configurations of  $O_2$ , namely bridge position, top position and hole position

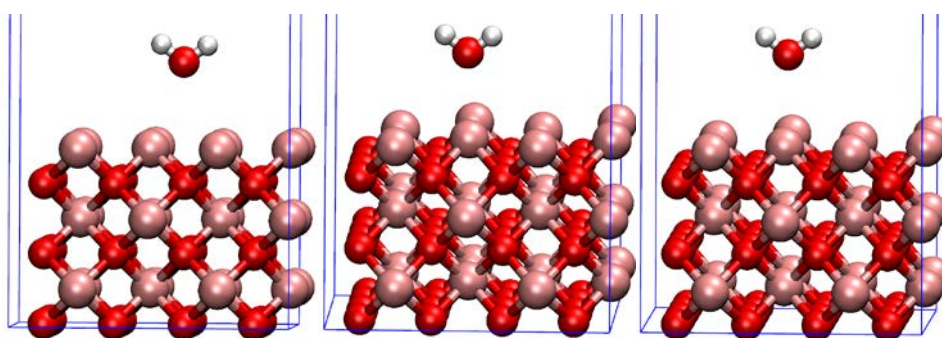


Figure 3: Three spatial configurations of  $H_2O$ , namely bridge position, top position and cave position

### 3. Results and Discussion

In the calculation, we found that  $O_2$  molecules can always dissociate and adsorb quickly on the surface of  $UO_2$ . Figure 4 shows the dissociation and adsorption of  $O_2$  molecules.  $H_2O$  molecules can be dissociated and adsorbed at both the hole site and the bridge site, but only molecular adsorption occurs at the top site. Figure 5 shows the dissociation and adsorption of  $H_2O$  molecules.

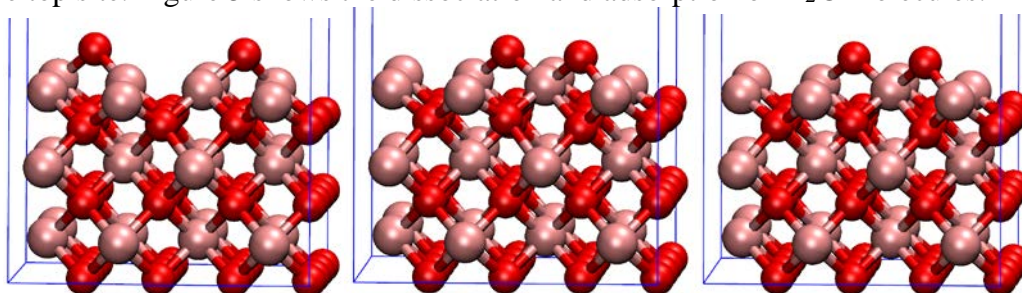


Figure 4: Three adsorption results of  $O_2$ , namely bridge position, top position and hole position

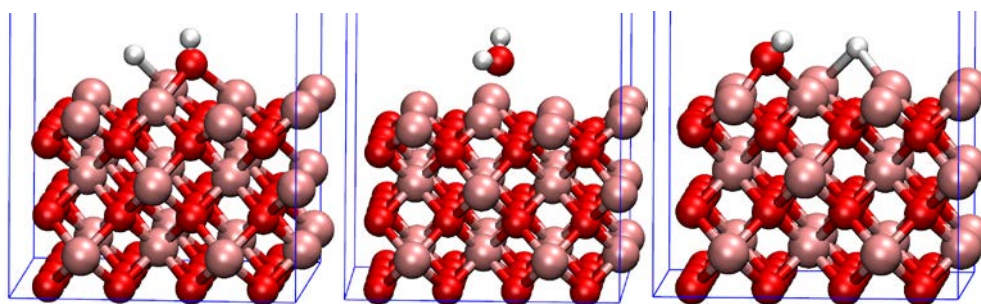


Figure 5: The three adsorption results of  $H_2O$ , namely bridge site, top site and cave site

After the  $O_2$  molecule dissociates, it forms a U-O bond with two U atoms, and is relatively stable.  $H_2O$  dissociates into one  $OH^-$  and one  $H^+$ .  $OH^-$  forms a U-OH- bond with the U atoms on the surface, while the U-H bond formed by  $H^+$  and U atoms is unstable.  $H^+$  moves on the surface of the unit cell.

By analyzing the U-O radial distribution function (RDF), as shown in Figure 3, there is an obvious peak in the first atomic layer and the second atomic layer, indicating that the interaction between O and U is strong, and U-O bonds are formed. There is a certain density between the first atomic layer and the second atomic layer, which indicates that the U-O bond is not very stable. There are U-O bond generation and U-O bond breakage. In Figure 4, the density between the first atomic layer and the second atomic layer is very large, and the UH bond is extremely unstable and easy to break. This indicates that after the dissociation of  $H_2O$ , the H atoms move continuously on the surface of the U unit cell. One point can be confirmed from the dynamic reaction process.

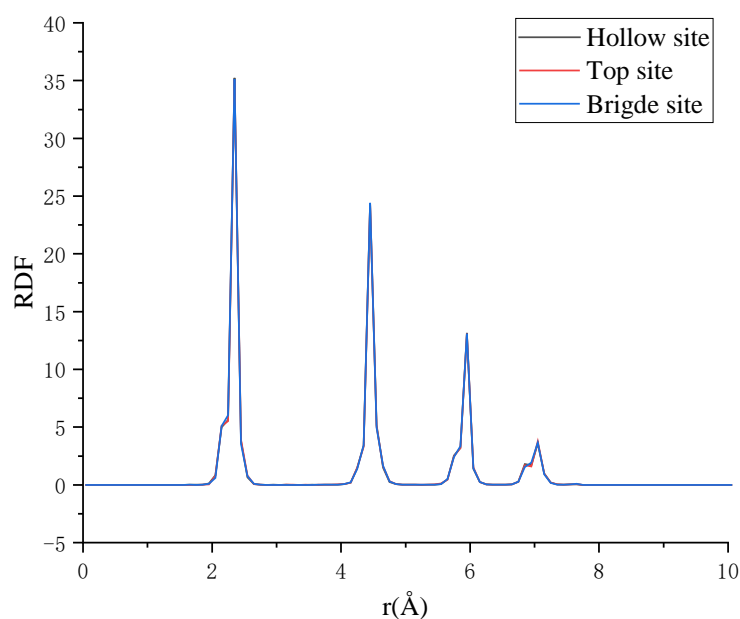


Figure 6: Radial distribution function of dissociative adsorption of  $O_2$  at the hollow site, top site, and bridge site

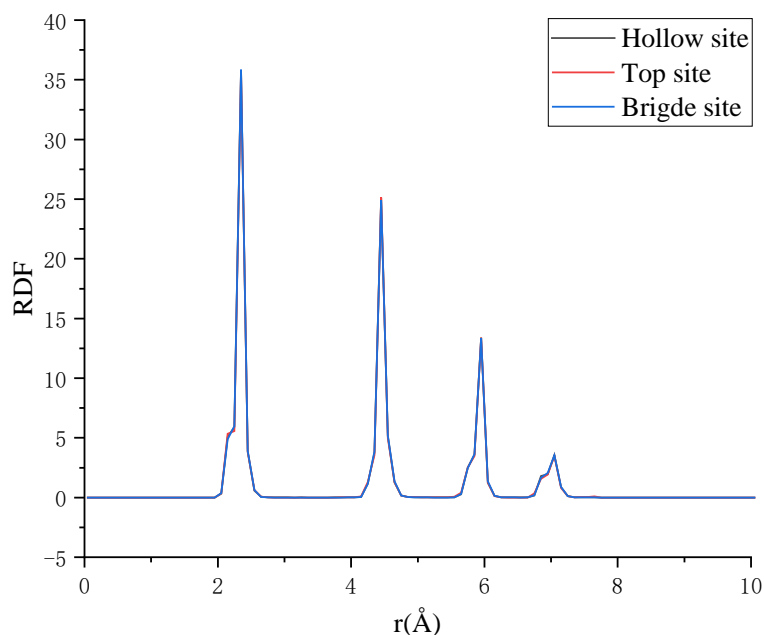


Figure 7: The radial distribution function of dissociation and adsorption of H<sub>2</sub>O at the hollow site, top site, and bridge site

#### 4. Conclusion

Through AIMD calculations, we found that O<sub>2</sub> molecules dissociated and adsorbed on the surface of UO<sub>2</sub>, H<sub>2</sub>O dissociated and adsorbed at the bridge and hole positions, and molecular adsorption occurred at the top position. Moreover, in dissociative adsorption, U-O is very stable, and the continuous movement of H atoms on the surface of the UO<sub>2</sub> unit cell makes the system after UO<sub>2</sub> oxidation unstable. Next, we will study the co-adsorption of O<sub>2</sub> and H<sub>2</sub>O on the surface of UO<sub>2</sub>.

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