

# First-principles study of water reacting with the (110) surface of uranium mononitride



Tao Bo <sup>a, b, c</sup>, Jian-Hui Lan <sup>b</sup>, Yao-Lin Zhao <sup>a, \*</sup>, Chao-Hui He <sup>a</sup>, Zhi-Fang Chai <sup>b</sup>, Wei-Qun Shi <sup>b, \*\*</sup>

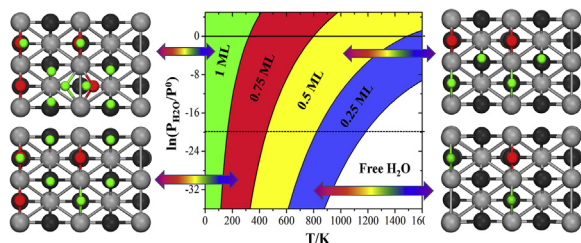
<sup>a</sup> School of Nuclear Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China

<sup>b</sup> Laboratory of Nuclear Energy Chemistry and Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> China Spallation Neutron Source (CSNS), Institute of High Energy Physics, Chinese Academy of Sciences, Dongguan 523803, China

## GRAPHICAL ABSTRACT

H<sub>2</sub>O Adsorption States on UN (110) Surface



## ARTICLE INFO

### Article history:

Received 14 January 2017

Received in revised form

5 May 2017

Accepted 19 May 2017

Available online 22 May 2017

### Keywords:

First principles

Uranium mononitride

Surface adsorption

Water

ab initio atomistic thermodynamic

## ABSTRACT

The adsorption and dissociation behaviors of water on the UN (110) surface have been investigated by using DFT + U method in combination with ab initio atomistic thermodynamic simulations. The most stable adsorption site for H, O, and OH adsorption is the uranium bridge site. For a water monomer, the adsorption energies are  $-0.90$ ,  $-3.23$ , and  $-4.46$  eV for the most stable molecular, partially dissociative, and completely dissociative adsorption, respectively. The dissociation of water from H<sub>2</sub>O to OH and H has a very small energy barrier, while from OH to O and H has a high energy barrier of 1.63 eV. The coverage dependence for molecular adsorption is not obvious, while for partially dissociative and completely dissociative adsorption, the coverage dependence is quite obvious. Besides, we have investigated the adsorption of water under different temperature and pressure conditions by using the “ab initio atomistic thermodynamic” method.

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## 1. Introduction

With the current global energy crisis, shortage of energy resources greatly hampers the development of global economy. One important way to solve this problem is to develop nuclear power. Uranium mononitride (UN) is considered to be one of the most promising fuel materials for the future Generation IV nuclear reactors [1]. Uranium mononitride fuel has many advantages as

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [zhaoyaolin@mail.xjtu.edu.cn](mailto:zhaoyaolin@mail.xjtu.edu.cn) (Y.-L. Zhao), [shiwq@ihep.ac.cn](mailto:shiwq@ihep.ac.cn) (W.-Q. Shi).

compared to the traditional uranium dioxide fuel, such as greater thermal conductivity [2,3], higher actinide density, higher melting point ( $\sim 2850$  °C) [4] and easier reprocessing [5]. However, UN materials still have some limitations, such as relatively low dissociation temperature [6,7] and incompatibility with oxygen and water [4,8]. Previous experimental studies [9–11] suggested that interaction between UN surface and oxygen can result in the oxide growth and the decrease of thermal conductivity. In addition, experimental studies [4,8,12] also suggested that UN interaction with water can result in the corrosion of nuclear fuels. Thus, the reactions of UN with oxygen and water affect a lot of processes in the nuclear fuel cycle such as fabrication and storage of nuclear fuels, and permanent disposal in deep geologic repository for spent fuel [13].

In the past decades, the UN has been widely investigated by using density function theory (DFT) and DFT + U methods [14–20]. However, only several studies have been performed on the UN surfaces. Bocharov et al. [21,22] studied the properties of N and U vacancies on the UN(001) surface and sub-surface and the incorporation of O atoms into these vacancies. In another work, Bocharov et al. [23] investigated the mechanism of UN oxidation by incorporation of O into N vacancies on the UN(001) and (110) surfaces. Zhukovskii et al. [24,25] investigated the properties of oxygen adsorption and dissociation on the UN(001) surface. Li et al. [26] investigated the H, C, and O adsorption on the UN(001) and (111) surfaces by using DFT + U method. They also studied the adsorption of single O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O on the UN(001) surface in another work [27]. In our recent studies [28], using the DFT + U method, we have thoroughly investigated the adsorption and dissociation of H<sub>2</sub>O on the UN(001) surface.

Based on the above introduction, the investigation of UN(110) surface with H<sub>2</sub>O by using DFT method has been rarely reported. In order to better understand the microscopic material properties, the initial stage of UN oxidation, and the fuel performance under different operating conditions, we plan to investigate the interaction mechanism between UN(110) surface and H<sub>2</sub>O by using the DFT + U method in this work. The research contents include: (1) the adsorption states of H, O, OH, and H<sub>2</sub>O monomer, (2) the surface reaction pathways of H, O diffusion and H<sub>2</sub>O dissociation, (3) the adsorption states of H<sub>2</sub>O at high coverages, (4) the water adsorption stability under different temperature and pressure.

## 2. Computational methodology

Our DFT calculations were performed using the Vienna ab initio Simulation Package (VASP) [29–31]. The projector augmented wave (PAW) approach [32,33] was used to represent the electron ion interaction. The electron exchange correlation functional was treated using the generalized gradient approximation (GGA) in the form proposed by Perdew-Burke-Ernzerhof formalism (PBE) [34]. The crystal structure of UN is face-centered cubic with sodium chloride type (space group *Fm3m*, No. 225). The lattice constant is calculated to be  $a = 4.931$  Å, which agrees well with the experimental value of 4.886 Å [35]. The periodic  $p(2 \times 2)$  slab consisting of six atomic monolayers (MLs) was used to simulate the UN(110) surface. Brillouin zone integration was calculated using  $2 \times 2 \times 1$  Monkhorst-Pack k-point meshes for the surface. A vacuum of 15 Å along the surface normal direction was set. The computations were performed with the cutoff energy of 550 eV. Spin-polarization was induced in all the investigated systems and the Gaussian electron smearing method with  $\sigma = 0.10$  eV was used. The H  $1s^1$ , N  $2s^2p^3$ , O  $2s^2p^4$ , and U  $5f^36s^2p^6d^17s^2$  were treated as valence electrons. We used antiferromagnetic (AFM) ordering of the magnetic moments in the overall system. The atomic positions were fully relaxed until the maximum force on each atom was smaller than 0.02 eV/Å.

DFT + U method was applied in our calculations in order to deal with strong on-site Coulomb repulsion of the 5f electrons for uranium element [1,36]. Lu et al. [36] concluded that the effective Hubbard parameter  $U_{\text{eff}} = 2.0$  eV achieves good agreement with experiments for the phonon density of states and phonon dispersions. Gryaznov et al. [1] found that the  $U_{\text{eff}} = 1.85$  eV achieves correctly the UN anti-ferromagnetic ordering, the magnetic moments and the unit cell volume. In our previous work [28], a value between the above two ( $U_{\text{eff}} = 1.90$  eV) was used to investigate the adsorption of water on the UN(001) surface. Thus, in this work, the value of  $U_{\text{eff}} = 1.90$  eV was used as the effective Hubbard parameter and the Coulomb  $U$  and the exchange energy  $J$  for the uranium element were set to be 2.40 and 0.50 eV, respectively. In order to evaluate the effects of van der Waals interaction on the adsorption of water on the UN(110) surface, the empirical dispersion corrections have been computed by using the DFT-D3 (BJ) method [37].

The adsorption energy,  $E_{\text{ad}}$ , is defined as

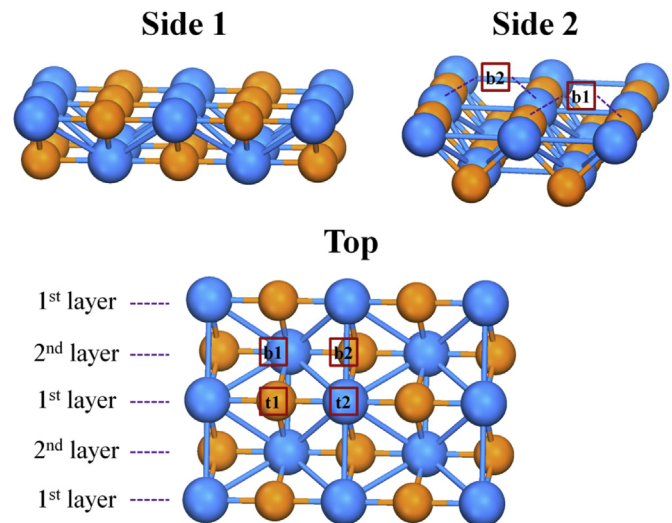
$$E_{\text{ad}} = E[\text{adsorbate/UN}] - E[\text{UN}] - E[\text{adsorbate}], \quad (1)$$

where  $E[\text{adsorbate/UN}]$  is the total energy of a UN(110) slab with adsorbed adsorbate;  $E[\text{UN}]$  is the total energy of the UN(110) slab;  $E[\text{adsorbate}]$  is the total energy of the free adsorbate. For the adsorption of H and O atoms,  $E[\text{H}]$  and  $E[\text{O}]$  represent half of the total energy of H<sub>2</sub> and O<sub>2</sub> molecules, respectively. Thus, for the adsorption of single H and O, the adsorption energy represents half of the adsorption energy for dissociative adsorption of H<sub>2</sub> and O<sub>2</sub>, respectively. The reaction paths were obtained by using the climbing image nudge elastic band (CI-NEB) method [38–40]. To study the interactions of water molecules with the UN(110) surface referring to real reaction conditions, it is significant to take into account water partial pressure and temperature. The “ab initio atomic thermodynamics” approach [41–43] was adopted to study the water adsorption properties. The detailed description of this method is given in the supporting information.

## 3. Results and discussion

### 3.1. Adsorption sites

Fig. 1 illustrates the schematic side and top views of the UN (110)



**Fig. 1.** Side and top views of the surface structure of UN (110) as well as possible adsorption sites (t for top, b for bridge). The uranium and nitrogen atoms are plotted in blue and yellow, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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