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

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\textbf{Graphical 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$_2$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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\section{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 \cite{1}. Uranium mononitride fuel has many advantages as...
compared to the traditional uranium dioxide fuel, such as greater thermal conductivity [2,3], higher actinide density, higher melting point (~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 decease 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 O2, CO2, and H2O 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 H2O on the UN(001) surface.

Based on the above introduction, the investigation of UN(110) surface with H2O 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 H2O by using the DFT + U method in this work. The research contents include: (1) the adsorption states of H, O, OH, and H2O monomer, (2) the surface reaction pathways of H, O diffusion and H2O dissociation, (3) the adsorption states of H2O 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 x 2) slab consisting of six atomic monolayers (MLs) was used to simulate the UN(110) surface. Brillouin zone integration was calculated using 2 × 2 × 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 used in all the investigated systems and the Gaussian electron smearing method with σ = 0.10 eV was used. The H 1s, N 2s+2p, O 2s+2p, and U 5f6s6p3d7s2 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 [36]. Liu et al. [36] concluded that the effective Hubbard parameter Ueff = 2.0 eV achieves good agreement with experiments for the phonon density of states and phonon dispersions. Gryzov et al. [1] found that the Ueff = 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 (Ueff = 1.90 eV) was used to investigate the adsorption of water on the UN(001) surface. Thus, in this work, the value of Ueff = 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, Ead, is defined as

\[ E_{ad} = E_{[adsorbate/UN]} - E_{[UN]} - E_{[adsorbate]}, \]

where \( E_{[adsorbate/UN]} \) is the total energy of a UN(110) slab with adsorbed adsorbate, \( E_{[UN]} \) is the total energy of the UN(110) slab; \( E_{[adsorbate]} \) is the total energy of the free adsorbate. For the adsorption of H and O atoms, \( E[H] \) and \( E[O] \) represent half of the total energy of H2 and O2 molecules, respectively. Thus, for the adsorption of single H and O, the adsorption energy represents half of the adsorption energy for dissociative adsorption of H2 and O2, 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)
surface as well as its possible adsorption sites. There are four adsorption sites on the UN (110) surface: nitrogen top (t1), uranium top (t2), nitrogen bridge (b1), and uranium bridge (b2) sites. The nitrogen bridge site (b1) represents the site between two surface nitrogen atoms, while the uranium bridge site (b2) represents the site between two surface uranium atoms.

3.2. Adsorption of H, O, OH, and H2O monomer on UN (110) surface

The interaction of water with UN surface is of particular interest from nuclear fuel cycle perspectives. In this section, we have investigated the adsorption of H, O, OH, and H2O monomer on the UN (110) surface by considering different initial configurations.

Fig. 2 illustrates top views of the stable adsorption structures of H, O, OH, and H2O on the UN (110) surface. The corresponding adsorption energies and the structure parameters are shown in Table S1 of the supporting information. The H, O, and OH are all treated as neutral species. For the adsorption of H atom, the most stable adsorption configuration is located at the uranium bridge site (Fig. 2b) with the H atom binding with two surface uranium atoms. The H-U bonds length are 2.31/2.30 Å and the adsorption energy is −0.75 eV. The adsorption configuration at the nitrogen top site (Fig. 2a) site is a metastable state. The adsorption energy is +0.05 eV and the H-N bond length is 1.04 Å. We also calculated the adsorption of H atom on the uranium top site. However, the adsorption configuration at the uranium top site is not stable because the hydrogen atom will move to an adjacent uranium bridge site without energy barrier. The diffusion pathway of H from uranium top site to uranium bridge site is given in Fig. S1 of the supporting information.

For the adsorption of O atom, the most stable adsorption configuration is located at the uranium bridge site (Fig. 2c) with the O atom coordinating with two surface uranium atoms. The O-U bonds length are 2.13/2.12 Å and the adsorption energy is −5.92 eV. The low adsorption energy represents strong interaction between UN (110) surface and O atom. It also represents that the dissociative adsorption of O2 on the UN (110) surface is very strong. In our previous work [28], we calculated the adsorption energy of O at the hollow site of the UN (001) surface to be −4.67 eV. Bocharov et al. [23] have reported the oxygen adsorption energies of −4.80 eV at the uranium top site of the UN (001) surface. We also calculated the adsorption of O atom on the nitrogen top site, uranium top site and nitrogen bridge site, respectively. However, these adsorption configurations are not stable because the oxygen atom will move to an adjacent uranium bridge site without energy barrier. The diffusion pathways of O from these three sites to uranium bridge site are given in Fig. S2 of the supporting information.

For the adsorption of OH, the most stable adsorption configuration (Fig. 2d) is characterized by the OH adsorbed at the uranium bridge site with the OH perpendicular to the surface. The O-U bonds length are 2.40/2.39 Å and the adsorption energy is −5.92 eV. From the above results we conclude that the most stable adsorption site for H, O, and OH adsorption is the uranium bridge site.

For H2O adsorption, we considered molecular, partially dissociative, and completely dissociative adsorption on the UN (110) surface. Fig. 2e–h illustrates the stable adsorption structures of H2O on the UN (110) surface. For molecular adsorption, the most stable adsorption configuration (Fig. 2e) is characterized by the oxygen atom of H2O coordinates with a surface uranium atom and a hydrogen atom of H2O binds with a surface nitrogen atom. The obtained U-O(H2) distance is 2.62 Å. A hydrogen bond with the length of 1.60 Å is formed between the H atom and the surface N atom. The adsorption energy for this configuration is −0.90 eV.

For partially dissociative adsorption with one OH and one H, we considered two stable adsorption structures which are shown in Fig. 2f and g. The most stable adsorption structure is shown in Fig. 2g. We can see that the OH and H are both adsorbed at uranium bridge sites. The obtained U-O(H) and U-H distances are 2.37/2.38 and 2.42/2.23 Å, respectively, and the adsorption energy for this configuration is −3.23 eV. For the adsorption structure as shown in Fig. 2f, the OH adsors at the uranium bridge site and the H adsorbs at the nitrogen top site. The obtained U-O(H) and H-N distances are 2.42/2.38 and 1.04 Å, respectively. The adsorption energy for this adsorption configuration is −2.34 eV, which is larger than that of configuration 2 g (−3.23 eV).

For completely dissociative adsorption of H2O, the most stable adsorption configuration is shown in Fig. 2h. The O atom and the H atoms are all adsorbed at uranium bridge sites with the U-O and U-H distances of 2.13/2.10, 2.28/2.25, and 2.24/2.24 Å, respectively. The adsorption energy for this configuration is −4.46 eV, which is much lower than those of molecular and partially dissociative adsorption. It is concluded that completely dissociative adsorption is the most stable one for H2O adsorption on the UN (110) surface.
In order to understand the effect of slab size on the adsorption properties, we calculated the adsorption of H, O, OH, and H$_2$O on the periodic (3 x 3) UN (110) surface. Fig. 3 illustrates top views of the stable adsorption structures of H, O, OH, and H$_2$O on the (3 x 3) UN (110) surface. The adsorption energies for H atom on the nitrogen top site (Fig. 3a) and uranium bridge site (Fig. 3b) are $-0.05$ and $-0.76$ eV, respectively, which are a little lower than those on the (2 x 2) surface. The length of the formed H-N and H-U bonds are 1.03 and 2.28/2.27 Å, respectively, which are comparable to those on the (2 x 2) surface. The adsorption energies for O and OH on the uranium bridge site (Fig. 3c and d) are $-6.34$ and $-6.43$ eV, respectively, which are a little lower than those on the (2 x 2) surface. For H$_2$O adsorption, the adsorption energy for molecular adsorption (Fig. 3e) is $-0.97$ eV, which is a little lower than that on the (2 x 2) surface ($-0.90$ eV). For partially dissociative adsorption with one OH and one H, the adsorption energies are $-2.44$ and $-3.37$ eV for configuration 3f (Fig. 3f) and configuration 3g (Fig. 3g), respectively, which are a little lower than those on the (2 x 2) surface ($-2.34$ and $-3.23$ eV). For completely dissociative adsorption of H$_2$O (Fig. 3h), the adsorption energy is $-4.90$ eV, which is a little lower than that on the (2 x 2) surface ($-4.46$ eV).

From the above results we conclude that the adsorption energies of H, O, OH, and H$_2$O on the periodic (3 x 3) UN (110) surface are just a little lower than those on the periodic (2 x 2) UN (110) surface. The small differences in adsorption energies result from the effect of adsorbate coverage. On the (3 x 3) UN (110) surface, the repulsive interactions between the adsorbates is small, which results in the lower adsorption energies. The calculated bonds length for H, O, OH, and H$_2$O adsorption on the periodic (3 x 3) UN (110) surface are comparable with those on the (2 x 2) UN (110) surface. The calculated surface energies for (2 x 2) and (3 x 3) UN (110) surfaces are 112.11 and 114.06 meV Å$^{-2}$, respectively. We can see that the two surface energies are very close. From the above discussion, we conclude that the (2 x 2) slab size is large enough for the investigation of H$_2$O adsorption on the UN (110) surface.

### 3.3. H, O diffusion and H$_2$O dissociation on UN (110) surface

On the basis of the stable H, O, and H$_2$O adsorption configurations calculated in the last section, we systematically investigated the probable reactions pathways of H, O diffusion and H$_2$O dissociation on the UN (110) surface. The minimum energy path for H diffusion and H$_2$O dissociation was modeled by the climbing image NEB method. The adsorption energies of the initial, transition, and final states and the corresponding structures are illustrated in Figs. 4–6.

Fig. 4 exhibits two calculated diffusion pathways of H atom on the UN (110) surface. Table S2 of the supporting information shows the energies, the reaction barriers, and the structure parameters of the adsorption configurations. These two diffusion pathways both

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**Fig. 3.** Optimized adsorption structures of (a, b) H, (c) O, (d) OH, and (e–h) H$_2$O on the (3 x 3) UN (110) surface. Color code as in Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4.** Potential energy profiles (eV) and structures of intermediates (E) and transition states (TS) for H diffusion on the UN (110) surface. Black numbers are energies of all the species and red numbers are energy barriers. Color code as in Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
start at one uranium bridge site (Ea1 and Eb1) and end at an
adjacent uranium bridge site (Ea2 and Eb3).

For the first diffusion pathway (Ea1 → Ea2), as shown in Fig. 4a,
the H atom is initially adsorbed at a uranium bridge site. The
adsorption energy for this configuration is −0.75 eV. Based on our
calculation, it needs to overcome an energy barrier of 1.55 eV for
the H atom to diffuse to an adjacent uranium bridge site. This
diffusion reaction is exothermic by 0 eV owing to the same
structure of the initial and final states.

The second diffusion pathway (Eb1 → Eb2 → Eb3) is investi-
gated which is shown in Fig. 4b. The H atom is initially adsorbed at a
uranium bridge site (Eb1). In the first diffusion process (Eb1 →
Eb2), it needs to overcome an energy barrier of 1.57 eV for the
atom to diffuse to an adjacent nitrogen top site. The energy barrier
is comparable to that of the first diffusion pathway (1.55 eV), for
the two reactions both need to overcome the U-H bond energy. At the
transition state (TSb1), the breaking U-H distance is 2.33/3.27 Å
and the newly formed N-H bond length is 1.45 Å. The adsorption en-
ergies for configuration Eb1 and Eb2 are −0.75 and 0.05 eV,
respectively. This reaction is endothermic by 0.80 eV. In the second
diffusion process (Eb2 → Eb3), the H atom diffuses from the nitro-
gen top site to an adjacent uranium bridge site. It needs to
overcome an energy barrier of 1.23 eV, which is lower than that of
the first diffusion process (1.57 eV). At the transition state (TSb2),
the breaking N-H distance is 1.54 Å and the newly formed U-H bond
length is 2.19 Å. The adsorption energy for configuration Eb3 is
−0.75 eV. This reaction is exothermic by 0.80 eV. At last, the
diffusion of H atom from Eb1 to Eb3 is exothermic by 0 eV and has
an overall energy barrier of 1.57 eV.

Fig. 5 exhibits calculated diffusion pathway of O on the UN (110)
surface. The energies, the reaction barriers, and the structure pa-
rameters of the adsorption configurations are shown in Table S3 of
the supporting information. The diffusion pathway (E1 → E2) is the
diffusion of O from the uranium bridge site to another uranium
bridge site. At the transition state (TS), the O coordinates with four
uranium atoms in the first layer and one uranium atom in the
second layer. The O-U distances are 2.91, 2.96, 2.89, 2.94, and 2.35 Å,
respectively. This diffusion pathway has a high energy barrier of
3.65 eV and the reaction heat is 0 eV. The high energy barrier for
this diffusion pathway is owing to the cleavage of the strong O-U
bonds.

Fig. 6 exhibits the reaction pathways of H2O dissociation on the
UN (110) surface. Table S4 of the supporting information shows the
energies, the reaction barriers, and the structure parameters of the
adsorption configurations. The process begins with the molecular
dissociation of H2O on the surface (E1) with the adsorption energy
of −0.90 eV. The next step is the H2O dissociation (E1 → E2), which
is exothermic by 1.44 eV and has a small energy barrier of 0.01 eV.
The energy barrier (0.01 eV) is really small and maybe within the
error of the calculation. It indicates that the dissociation of H2O on
the UN (110) surface takes place easily. The bond length of N-H is
shortened from 1.60 Å in E1 via 1.47 Å in TS1 to 1.04 Å in E2, while
the distance of O-H1 is elongated from 1.06 Å in E1 via 1.11 Å in TS1
to 3.09 Å in E2. The next step (E2 → E3) is the diffusion of H
atom from the nitrogen top site to the neighboring uranium bridge
site. In the transition state (TS2), the bond length of N-H1 is 1.45 Å,
which is 0.41 Å longer than that of E2. This reaction is exothermic
by 0.89 eV, which is comparable to that of the diffusion of H atom
in the previous calculation without OH accompanying (0.80 eV).
However, the energy barrier of this reaction (0.89 eV) is lower than
that in the previous calculation without OH accompanying
(1.23 eV). The configuration (E3) is the most stable structure of
partially dissociative adsorption of H2O on the UN (110) surface.
The third reaction (E3 → E4) is the dissociation of OH into O and H
at the uranium bridge sites. The bond length of O-H2 is elongated
from 0.97 Å in E3 via 1.93 Å in TS3 to 5.03 Å in E4. This reaction is
exothermic by 1.23 eV and has an energy barrier of 1.63 eV. The
configuration (E4) is the most stable structure of completely dissociative adsorption of H$_2$O.

3.4. Adsorption of H$_2$O at higher coverages on UN (110) surface

In this section, we calculated the molecular, partial dissociative, mixed dissociative, and completely dissociative adsorption of two, three, and four water molecules in order to get a better understanding of water adsorption at different coverages on the UN (110) surface. Fig. 7 illustrates the optimized most stable adsorption structures of two, three, and four water molecules on the UN (110) surface. The adsorption energies and the detailed geometrical parameters are listed in Table S5 of the supporting information.

We first discuss the adsorption of two water molecules. Molecular adsorption and partial, mixed, and completely dissociative adsorption of two water molecules are investigated. The adsorption energy is $-2.05 \text{ eV}$ for the most stable molecular adsorption configuration as shown in Fig. 7a. The two H$_2$O coordinate with two surface U atoms with the U-O(H2) distances of 2.66 and 2.60 Å, respectively. A hydrogen bond with the length of 2.10 Å is formed between the two water molecules. Fig. 7b shows the most stable partial dissociative adsorption configuration with two hydroxyl ions and two hydrogen atoms. The two OH and two H are adsorbed at four uranium bridge sites with the U-O(H) and U-H distances of 2.36/2.34, 2.36/2.34, 2.24/2.24, and 2.24/2.24 Å, respectively. The adsorption energy for this configuration is $-6.26 \text{ eV}$. The most stable mixed dissociative adsorption configuration with one OH, one O, and three H is shown in Fig. 7c. In this case, the OH and O are adsorbed at two uranium bridge sites with the U-O and U-O(H) distances of 2.36/2.34 and 2.12/2.12 Å, respectively, and the three H are adsorbed at two uranium bridge sites and one nitrogen top site, respectively. The adsorption energy is $-7.03 \text{ eV}$ for this configuration. In the completely dissociative adsorption configuration (Fig. 7d), the two O are adsorbed at two uranium bridge sites with the U-O distances of 2.12/2.12 and 2.12/2.12, respectively, and the four H are located at two uranium bridge sites and two nitrogen top sites, respectively. The adsorption energy for this configuration is $-7.48 \text{ eV}$. We can see that completely dissociative adsorption mode is the most preferable one at the coverages of 2/4 ML on the UN(110) surface.

The molecular and dissociative adsorptions of three water molecules are also investigated here. Fig. 7e shows the most stable molecular adsorption configuration, where all the three H$_2$O adsorb on three surface U atoms with the U-O(H2) distances of 2.62, 2.66, and 2.62 Å, respectively. The calculated adsorption energy for this configuration is $-2.95 \text{ eV}$. In the most stable partial dissociative adsorption configuration with three OH and three H (Fig. 7f), the three OH are adsorbed at three uranium bridge sites with the U-O(H) distances of 2.62, 2.66, and 2.62 Å, respectively, and the three H are located at one uranium bridge site and two nitrogen top sites, respectively. The calculated adsorption energy for this configuration is $-7.80 \text{ eV}$. In the most stable mixed dissociative adsorption configuration with one OH, two O, and five H (Fig. 7g), the OH and the two O are adsorbed at three uranium bridge sites with the U-O(H) and U-O distances of 2.35/2.40, 2.13/2.13, and 2.13/2.13 Å, respectively, and the five H are adsorbed at one uranium bridge site and four nitrogen top sites, respectively. The calculated adsorption energy for this configuration is $-9.03 \text{ eV}$. In the most stable completely dissociative adsorption configuration with three O and six H (Fig. 7h), the three O are adsorbed at three uranium bridge sites with the U-O distances of 2.07/2.18, 2.08/2.12, and 2.14/2.10 Å, respectively, and the six H are adsorbed at four nitrogen top sites, one uranium bridge site, and one uranium top site, respectively. A H-H bond of 1.63 Å is formed between the H adsorbed at the uranium top site and the H adsorbed at the uranium bridge site. The calculated adsorption energy is $-8.14 \text{ eV}$ for this configuration. We can see that mixed dissociative adsorption is the most preferable mode at the water coverage of 3/4 ML.

For four water molecules located on the surface, we also provided the most stable molecular and dissociative adsorption configurations. Fig. 7i shows the most stable molecular adsorption configuration, where all the four water molecules adsorb on surface U atoms with the U-O(w) distances of 2.65, 2.70, 2.60, and 2.64 Å, respectively. Two hydrogen bonds with the length of 2.04 and

![Fig. 7. Optimized (a, e, i) molecular, (b, f, j) partial dissociative, (c, g, k) mixed dissociative, and (d, h, l) completely dissociative adsorption structures of (a, b, c, d) two, (e, f, g, h) three, and (i, j, k, l) four water molecules on the UN (110) surface. Color code as in Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
1.96 Å are formed among the four water molecules. The calculated adsorption energy for this configuration is $-4.13$ eV. In the most stable partial dissociative adsorption configuration with four OH and four H (Fig. 7), all the four OH are adsorbed at uranium bridge sites with the U-O(H) distances of 2.36/2.43, 2.39/2.40, 2.36/2.43, and 2.39/2.40, respectively, and all the four H adsorb at nitrogen top sites. The calculated adsorption energy for this configuration is $-8.97$ eV. In the most stable mixed dissociative adsorption configuration with three OH, one O, and five H (Fig. 7k), the three OH and the O are adsorbed at four uranium bridge sites, and the five H are adsorbed at four nitrogen top sites and one uranium bridge site, respectively. The calculated adsorption energy for this configuration is $-9.54$ eV. In the most stable completely dissociative adsorption configuration with four O and eight H (Fig. 7l), the four O are adsorbed at four uranium bridge sites with the U-O distances of 2.06/2.06, 2.06/2.06, 2.05/2.05, and 2.05/2.06, respectively, and the eight H are adsorbed at four nitrogen top sites and four uranium top sites, respectively. The calculated adsorption energy for this configuration is $-2.46$ eV. We can see that the mixed dissociative adsorption with three OH, one O, and five H is the most preferable adsorption mode at the water coverage of 1 ML.

For molecular adsorption on the UN(110) surface, the average adsorption energies of one, two, three, and four water molecules are $-0.90$ (1/4 ML), $-1.03$ (2/4 ML), $-0.98$ (3/4 ML), and $-1.03$ (1 ML) eV, respectively. We can see that the coverage dependence is not obvious for molecular adsorption. The average adsorption energies for partial dissociative adsorption are $-3.23$ (1/4 ML), $-3.13$ (2/4 ML), $-2.60$ (3/4 ML), and $-2.24$ (1 ML) eV, respectively. We can see that the average adsorption energy decreases slightly as the coverage increases from 1/4 to 2/4 ML but decreases remarkably from 2/4 to 1 ML. The average adsorption energies for completely dissociative adsorption are $-4.46$ (1/4 ML), $-3.74$ (2/4 ML), $-2.71$ (3/4 ML), and $-0.62$ (1 ML) eV, respectively. One can see that the average adsorption energy decreases remarkably from 1/4 ML to 1 ML. It can be conclude that the coverage dependence is quite obvious for partial dissociative and completely dissociative adsorption, which results from the lateral electrostatic repulsive interactions among the adsorbed species and steric effect. Furthermore, our calculations reveal that the most preferable adsorption modes are completely dissociative adsorption at the coverages of 1/4 and 2/4 ML, while mixed adsorption at the coverages of 3/4 and 1 ML on the UN(110) surface.

3.5. Water adsorption from ab initio atomistic thermodynamics

3.5.1. Water adsorption with pressure and temperature

We next go on to analyze the water adsorption on the UN(110) surface under different pressure and temperature conditions by using the “ab initio atomistic thermodynamics” method. As illustrated in Eqn (56) of the supporting information, $\Delta G$ can be used to test the stability of UN(110) surface with adsorption of nH$_2$O under different pressure and temperature conditions, and more negative $\Delta G$ indicates a more stable structure. On the basis of the most stable adsorption structures at different coverages, we plotted $\Delta G$ as a function of $p_{H_2O}$ (Fig. 8) and T (Fig. 9), respectively. The most stable adsorption states for water at the coverages of 1/4 (1H$_2$O), 2/4 (2H$_2$O), 3/4 (3H$_2$O), and 1 (4H$_2$O) ML are considered here.

Firstly, we investigated the effect of H$_2$O partial pressure ($p_{H_2O}$) on the adsorption properties by taking fixed temperatures of 300 K, 600 K, and 900 K respectively. The water partial pressure ($p_{H_2O}$) plays an important role in adsorption behaviors because it reflects the H$_2$O equilibrium concentration in the gas phase. Fig. 8a–c illustrates the relationship between $\Delta G$ and $ln(p_{H_2O}/p^0)$ for water adsorption on the UN(110) surface at 300 K, 600 K, and 900 K, respectively. The more negative the $\Delta G$, the more stable the adsorbed system. For water adsorption at 300 K (Fig. 8a), the adsorption of three H$_2$O (3/4 ML) is the most stable case within $ln(p_{H_2O}/p^0) < -2$. For higher H$_2$O partial pressure within $ln(p_{H_2O}/p^0) > -2$, the adsorption of four H$_2$O (1 ML) becomes the most stable case, indicating that the H$_2$O coverage increases. For water adsorption at 600 K (Fig. 8b), the adsorption of two H$_2$O (2/4 ML) is the most stable case within $ln(p_{H_2O}/p^0) < -9$, and the adsorption of three H$_2$O (3/4 ML) is the most stable case within $ln(p_{H_2O}/p^0) > -9$, indicating that the H$_2$O coverage increases. We can see that for water adsorption at 300 K and 600 K, the $\Delta G$ is almost always negative within the whole range of H$_2$O partial pressure for the four adsorption structures, indicating that the adsorption of H$_2$O on the UN(110) surface is quite favorable below 600 K. For water adsorption at 900 K (Fig. 8c), the adsorption of one H$_2$O (1/4 ML) is the

Fig. 8. The relationship between the Gibbs free energy of adsorption ($\Delta G$) and H$_2$O partial pressure at (a) 300 K, (b) 600 K, and (c) 900 K, respectively. nH$_2$O represents the most stable adsorption state of n water.
most stable case within \( \ln(p_{\text{H}_2\text{O}}/p_0) < -17 \). As the increasing of H\(_2\)O partial pressure, the adsorption configuration with two H\(_2\)O becomes the most stable case within \(-17 < \ln(p_{\text{H}_2\text{O}}/p_0) < 3\). For higher H\(_2\)O partial pressure within \(\ln(p_{\text{H}_2\text{O}}/p_0) > 3\), the adsorption of three H\(_2\)O is the most stable case. From the above results it can be seen that increasing H\(_2\)O partial pressure can strengthen the stability of all the adsorption structures and increase the water coverage on the UN(110) surface.

Secondly, we investigated the relationship between \( \Delta G \) and temperature by taking a fixed H\(_2\)O partial pressure, and the data of \( p_{\text{H}_2\text{O}} = 1 \times 10^{-10} \) atm (\( \ln(p_{\text{H}_2\text{O}}/p_0) = -23 \)) was used for discussion. Apart from H\(_2\)O partial pressure, temperature also plays a significant role in the water adsorption properties. Fig. 9 illustrates the relationship between \( \Delta G \) and temperature for water adsorption on the UN(110) surface at \( \ln(p_{\text{H}_2\text{O}}/p_0) = -23 \). The adsorption structure with four H\(_2\)O molecules (1 ML) is the most stable case with \( T < 150 \) K. When the temperature is increased to the range of 150 K < \( T < 420 \) K, the adsorption configuration with three H\(_2\)O molecules (3/4 ML) becomes the most stable case, indicating that the H\(_2\)O coverage decreases. For higher temperatures (420 K < \( T < 770 \) K), the H\(_2\)O coverage continues to decrease and the adsorption structure with two H\(_2\)O molecules (2/4 ML) becomes the most stable case. For \( T > 770 \) K, the most stable case is the surface adsorbed with one H\(_2\)O molecule (1/4 ML). From the above results it can be conclude that increasing temperature can decrease the stability of all the adsorbed system and decrease the water coverage on the UN(110) surface.

3.5.2. Phase diagram of stable water coverage

It is meaningful and important experimentally to adjust both H\(_2\)O partial pressure and temperature at one time for practical goals. Thus, in this section, we investigated the stable water adsorption states on the UN(110) surface as a function of both H\(_2\)O partial pressure and temperature. As shown in Fig. 10, we plotted the pressure-temperature phase diagram for H\(_2\)O adsorption at different coverages. The most stable adsorption states for water at the coverages of 1/4 (1H\(_2\)O), 2/4 (2H\(_2\)O), 3/4 (3H\(_2\)O), and 1 (4H\(_2\)O) ML are considered here.

The phase diagram has five regions. The blue region represents the range of H\(_2\)O partial pressure and temperature, in which the adsorption structure with the water coverage of 1/4 ML is the most stable case. The yellow, red, and green regions correspond to the coverages of 2/4, 3/4, and 1 ML, respectively. Below these regions, the water-free surface is possible. We can see that the water coverage decreases from 1 ML to 1/4 ML gradually with the increase of temperature. For example, at H\(_2\)O partial pressure of \(\ln(p_{\text{H}_2\text{O}}/p_0) = -20\), the saturated water adsorption (1 ML) has the temperature range up to 160 K and the complete desorption of water from the surface happens when the temperature rises to 1100 K. The phase diagram shows clearly that water desorption temperature increases with increasing H\(_2\)O partial pressure. By phase diagram the water coverage on the UN(110) surface can be determined under a certain H\(_2\)O partial pressure and temperature. Therefore, the water adsorption phase diagram is informative and it is possible to adjust the balance between temperature and H\(_2\)O partial pressure for practical uses.

4. Conclusions

In this work, we studied the adsorption and dissociation behaviors of water on the UN(110) surface by using DFT + U method in combination with ab initio atomistic thermodynamic simulations. From our calculations, 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 completely adsorption exhibits the lowest adsorption energy, while the molecular adsorption exhibits the highest adsorption energy.

According to our calculations, the diffusion pathway of H from the uranium bridge site directly to the adjacent uranium bridge site has an energy barrier of 1.55 eV, while from the uranium bridge site to the adjacent nitrogen top site has an energy barrier of 1.57 eV. The diffusion pathway of O from the uranium bridge site to the adjacent uranium bridge site has a high energy barrier of 3.65 eV, indicating the strong stability for O atom adsorption. The dissociation of water from H\(_2\)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. For water adsorption at high coverages, the coverage dependence for molecular adsorption is not obvious, while for partially dissociative and completely dissociative adsorption, the coverage dependence is quite obvious. Besides, by using the “ab initio atomistic thermodynamic” method, we found that the adsorption of H\(_2\)O on the UN(110) surface is quite favorable below 600 K, leading to the dissolution and corrosion of the UN fuel materials. This work can help to understand the interaction mechanism between UN(110) surface and water in the
environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jnucmat.2017.05.026.

References


