



Chemisorption of a molecular oxygen on the UN(0 0 1) surface: *Ab initio* calculations

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ABSTRACT

The results of DFT GGA calculations on oxygen molecules adsorbed upon the (0 0 1) surface of uranium mononitride (UN) are presented and discussed. We demonstrate that O₂ molecules oriented parallel to the substrate can dissociate either (i) spontaneously when the molecular center lies above the surface hollow site or atop N ion, (ii) with the activation barrier when a molecule sits atop the surface U ion. This explains fast UN oxidation in air.

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1. Introduction

The uranium mononitride (UN), which possesses a rock salt structure and metallic nature, is an advanced material for the non-oxide nuclear fuel considered as a promising candidate for the use in Generation-IV fast nuclear reactors. UN reveals several advantages over a traditional UO₂-type fuel (e.g., higher thermal conductivity and metal density). However, one of important problems with actinide nitrides is their effective oxidation in contact with oxygen which can affect nuclear fuel performance [1].

There was a series of *ab initio* density functional theory (DFT) calculations published in last 10 years on pure and defective UO₂ (e.g., [2–10]). Similar calculations on the UN appeared only recently [11–16]. In our recent papers, we studied both the structure of a perfect UN(0 0 1) surface [17] and chemisorption of oxygen atoms upon it [18]. These DFT calculations were performed using the two quite different computer codes: VASP 4.6 [19], with plane wave basis set (BS), and CRYSTAL-06 [20], with the BS of localized atomic orbitals (LCAO approach). In both cases we have applied the non-local exchange-correlation functional by Perdew–Wang-91 (PW91), that is, the generalized gradient approximation (GGA) [21]. The results of these two different methods reveal good agreement [17,18] which supports their reliability. A strong *chemisorption* was observed for a single O atom interaction with the UN surface (~7 eV is the binding energy atop the surface U ion) [18] which is typical for traditional metallic surfaces (cf. ~10 eV per adatom bound on the close-packed Al surfaces [22]). However, to shed more light on the UN oxidation mechanism, we study theoretically in this paper the interaction of *molecular* oxygen with the same defectless UN(0 0 1) surface. The key questions are: whether the O₂ dissociation upon the surface is energetically possible, which adsorption sites are optimal for this, and whether it can occur spontaneously, without energy barrier. These are

important issues for understanding the mechanism of the oxidation of uranium nitride in air.

2. Theoretical

We have employed the VASP 4.6 code [19] with the relativistic PAW pseudopotentials representing the core electrons of U (6s²6p⁶6d²5f²7s² valence shell), N (2s²2p³) and O (2s²2p⁴) atoms as well as the non-local PW91 exchange correlation functional [21]. The cut-off energy has been chosen 520 eV. We have applied the Monkhorst–Pack scheme [23] with 4 × 4 × 1 *k*-point mesh in the Brillouin zone (BZ). When modeling the UN(0 0 1) surface, we have used the same 3D symmetric slabs as previously [17,18] consisting of five non-polar layers, containing alternating U and N atoms, separated by large vacuum gaps along the *z*-axis (~36 Å) and thus excluding the direct interaction of oxygen molecules from the neighboring slabs. The lattice constant (4.87 Å) optimized for the bulk has been used in all our slab calculations accompanied by a full structure optimization. The DFT GGA calculations suggest *ferromagnetic* ground state [24] of UN which contradicts the experimental observations of AFM phase at low temperatures [1]. Our test calculations [17] have confirmed that the FM phase is energetically more favorable also for the UN slab.

For simulation of the chemisorption of oxygen molecule, we have used mainly the 2 × 2 extended surface supercell (containing 20 U cations and 20 N anions), similarly to the previous study on chemisorption of an atomic oxygen [18]. The periodic adsorbate distribution corresponds to the molecular coverage of 0.25 ML (or atomic O coverage of 0.5 ML). To reduce computational efforts, we have used a symmetric two-sided arrangement of oxygen molecules on both surfaces of the slab. The energy gain E_{gain} per oxygen atom in the adsorbed molecule (O₂)_{ads} arising after approach of the O₂ molecule towards the UN surface has been calculated as

$$E_{\text{gain}} = \frac{1}{4} (E^{\text{UN}} + 2E^{\text{O}_2} - E^{\text{O}_2/\text{UN}}), \quad (1)$$

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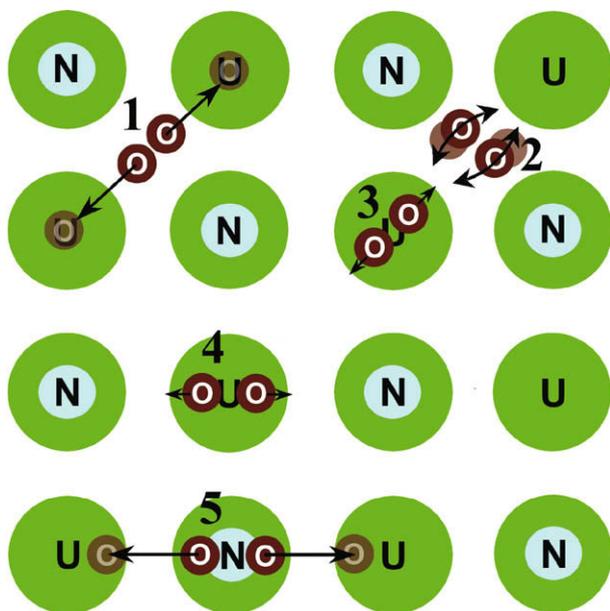


Fig. 1. Schematic view of five different horizontal configurations for the O_2 molecule adsorption on UN surface: (1) atop the hollow site oriented towards the nearest surface U ions, (2) atop the hollow site oriented towards the nearest surface N ions, (3) atop the surface U ions oriented towards the next-nearest surface U ions, (4) atop the surface U ions oriented towards the nearest surface N ions, (5) atop the surface N ions oriented towards the nearest surface U ions. We show, using arrows, that molecule spontaneous dissociation can occur when O_2 is located either atop the hollow site (1) or atop ion N (5).

where $E_{O_2/UN}^0$ is the total energy of a fully relaxed $O_2/UN(001)$ slab for several configurations of $(O_2)_{ads}$ upon the substrate (with a center of molecule atop the corresponding surface site as shown in Fig. 1), E_2^0 and E^{UN} the total energies of an isolated oxygen molecule in the ground (triplet) state and of a pure relaxed slab, respectively. The factor $1/4$ before brackets appears since the substrate is modeled by a slab containing the two equivalent surfaces with $(O_2)_{ads}$ positioned symmetrically relatively to both slab surfaces whereas each molecule before and after dissociation contains two oxygen atoms. Similar analysis was earlier performed by us for various O_2/Al interfaces [22].

To compare the binding energy (E_{bind}) for the atomic oxygen adsorption atop the surface uranium atom calculated by us earlier [18] with the E_{gain} per dissociated oxygen adatom (Table 1), one should add about half the binding energy of oxygen molecule to the latter energy. The calculated E_{bind} for a free O_2 molecule in the triplet state is 6.06 eV and a bond length of 1.31 Å (cf. with the experimental values of 5.12 eV and 1.21 Å [25], respectively).

Table 1

The calculated energy gains (E_{gain} , Eq. (1)) and dissociation E_{diss} energies (eV), geometry (z , Δz) and charges (q) for configurations of molecular and spontaneous dissociative chemisorption of oxygen molecule above the UN(001) substrate. Numbers in brackets correspond to the configurations shown in Fig. 1.

Position		E_{gain} per O atom, eV	z^a , Å	E_{diss} , eV	$q(O)$, e	$q(U1^b)$, e	$q(U2^c)$, e	$q(N^d)$, e	$\Delta z^e(U1)$, Å	$\Delta z^e(U2)$, Å	$\Delta z^e(N)$, Å
Hollow (1)	Molecular adsorption	1.185	1.893	–	–0.465	1.913	1.762	–1.533	–0.0496	–0.0496	0.02498
	After dissociation	4.21	1.957	3.025	–0.978	2.053	1.978	–1.577	0.075	0.068	–0.133
Atop U	Towards next-nearest U (3)	2.15	2.18	–	–0.5905	2.042	1.836	–1.6065	0.176	–0.048	–0.096
	Towards nearest N (4)	2.33	2.14	–	–0.578	2.0485	1.827	–1.6248	0.123	–0.051	–0.106
Atop N (5)	Molecular adsorption	0.82	2.020	–	–0.5685	1.8675	1.8322	–1.3537	–0.0496	–0.0496	0.025
	After dissociation	4.00 ^f	1.955	3.18	–0.979	2.115	1.876	–1.580	0.073	0.021	–0.201

^a z is the height of O atoms respectively the non-relaxed UN substrate.

^b U1 the nearest surface U ion.

^c U2 the next-nearest surface U ion.

^d N the nearest surface N ion.

^e Δz the additional vertical shifts of the same surface ions from their positions in the absence of adsorbed oxygen.

^f 4.40 eV for 3×3 extended surface supercell.

3. Main results

When modeling the molecular adsorption, we have analyzed different configurations of an O_2 molecule in the triplet state on the UN(001) substrate. Vertical orientations of the molecule atop the surface N or U ions have been found metastable with respect to molecule reorientation to the horizontal configuration, parallel to the surface. We have estimated both the energy gain of molecular adsorption using Eq. (1) and the O_2 dissociation energy (for some configurations), i.e., the difference of the total energies of a slab with an oxygen molecule before and after dissociation, when the two O atoms in the triplet state which sit atop the two nearest surface U ions (Table 1).

3.1. Spontaneous dissociation of O_2 molecules

We have found that a spontaneous, barrierless O_2 dissociation indeed takes place in the two cases: when the molecular center is atop either (i) a hollow site or (ii) surface N ion, with the molecular bond directed towards the two nearest surface U ions (the configurations 1 and 5 in Fig. 1, respectively). The relevant dissociation energies E_{diss} are given in Table 1, along with other parameters characterizing the atomic relaxation and the Bader charge distribution. To estimate energy gain for intermediate molecular adsorption in these two configurations (as present in Table 1) we have fixed the O_2 bond length as in a gas phase allowing the molecule to relax only along a distance from the surface. Geometry and charges for the configurations 1 and 5 after dissociation (Table 1) are in general similar to those obtained in our previous study [18] for UN(001) substrate covered by chemisorbed O atoms, e.g., surface U atoms beneath the oxygen adatom after dissociation are shifted up in both configurations. An increase of the surface supercell size from 2×2 up to 3×3 results in the 10% growth of the E_{gain} due to a reduced repulsion between the periodically distributed adatoms (Table 1).

We have also identified two other configurations of adsorbed oxygen molecules where the dissociation is energetically possible but with the energy barrier: (i) atop the hollow site when a molecular bond is oriented towards the nearest N ions (the configuration 2 in Fig. 1) and (ii) atop the surface U ion (for any molecular orientation, e.g., the configurations 3 and 4 in Fig. 1). For the configuration 2, we have observed the orientation instability of the adsorbed molecule which easily rotates, e.g., towards the surface U ion with further dissociation. The configurations 3 and 4 could be characterized as rather metastable UO_2 quasi-molecules due to a strong bonding between all three atoms (Fig. 2c) and since the corresponding U ion is noticeably shifted up from its initial positions on surface (Table 1). Meanwhile, the dissociation of $(O_2)_{ads}$ molecule in the configuration 3 is energetically possible but only after overcoming the small (~ 0.3 eV) activation energy barrier.

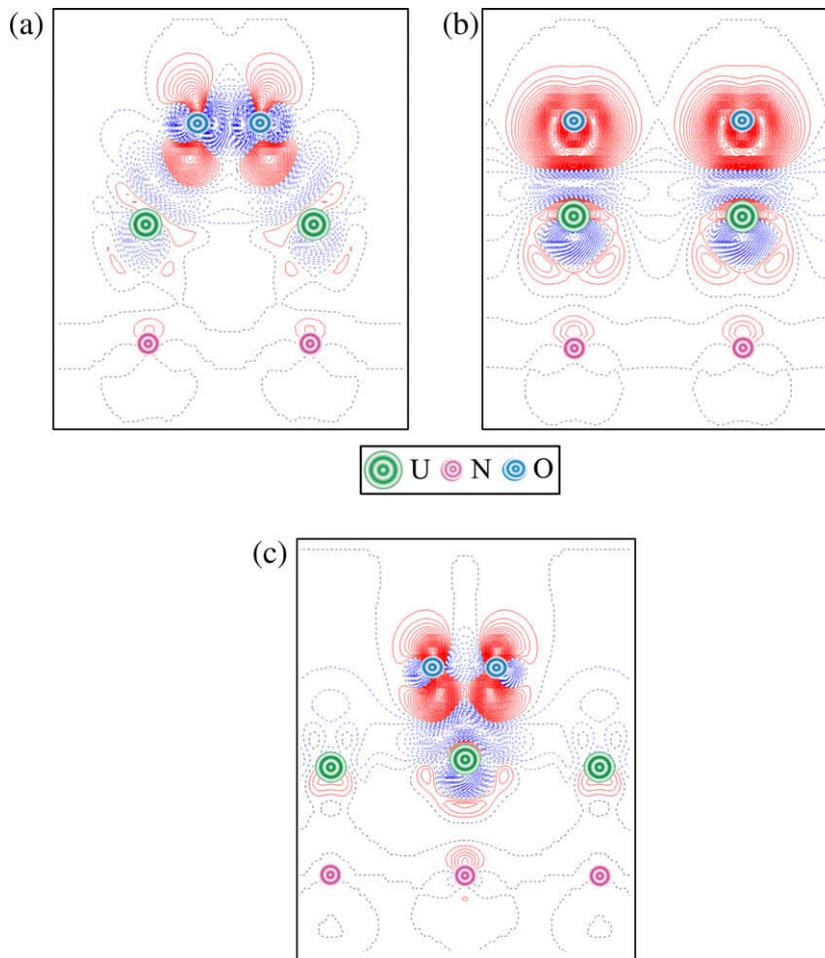


Fig. 2. The difference electron density maps $\Delta\rho(r)$ (the total density of the interface minus the sum of densities of substrate and adsorbate with optimized interfacial geometry) for (a) the O_2 molecule upon the hollow position oriented to the nearest surface U ions, (b) after its dissociation in the configuration 1 (Fig. 1) with O atoms atop the surface U ions and (c) for the O_2 molecule atop the surface U ion in the configuration 3 (Fig. 1). Solid (red) and dashed (blue) isolines correspond to positive (excess) and negative (deficiency) electron density, respectively. Isodensity increment is $0.003 e \text{ \AA}^{-3}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Charge redistribution analysis

Adsorption of an O_2 molecule (in the triplet state) is accompanied by the charge transfer of $\sim 1 e$ (per molecule) from the substrate (Table 1). In Fig. 2 we analyze the difference electron charge redistributions for three configurations of horizontally oriented (O_2)_{ads} upon the surface: (a) molecule adsorbed upon the hollow site (the configuration 1, Fig. 1), (b) molecule dissociated from this configuration with O adatoms located atop the nearest surface U ions, and (c) molecule adsorbed upon the surface U ion (the configuration 3). Spontaneous O_2 dissociation and thus a smooth transition from the charge distribution (a) to (b) can be explained by continuous areas of the electron density (Fig. 2a) parallel to the surface which may be considered as *dissociation channels*, analogously to the density plot for a molecular oxygen upon the Al substrate [22]. After dissociation each O adatom contains an extra charge of $\sim 1 e$, i.e., transforms into O^- ion in the triplet state (Fig. 2b). In contrast, when considering the molecular configuration 3, these *dissociation channels* are transformed into *dissociation barriers* (Fig. 2c). Simultaneously, we observe considerably higher electron density, indicating a kind of UO_2 quasi-molecule with a strong bonding between the O_2 molecule and surface U atom beneath. Thus, difference between the electron density plots presented in Fig. 2a and c can explain different dissociation abilities of O_2 molecule in the configurations 1 and 3 (Fig. 1).

3.3. Electronic densities of states (DOS)

For the same adsorbate configurations considered above, we have constructed the total and projected densities of states (DOS) (Fig. 3). Molecular adsorption in these configurations leads to appearance of the specific *oxygen bands* as compared to those for oxygen adatoms upon UN surface [18] and O atom substituted for a host N ion in UN bulk [15]. For a molecular oxygen atop the hollow position (Fig. 3a), O 2p peak is observed at $-1 eV$ overlapping with the U 5f and 6d bands. After O_2 dissociation (Fig. 3b) this peak disappears being replaced by the broad two-peak band in the region of the N 2p valence band (-2 to $-5 eV$), similarly to the DOS for oxygen adatoms on UN(001) substrate [18]. Some differences are also noticeable between the corresponding U 5f and 6d peaks in the spectral range above $-1 eV$ (cf. Fig. 3a and b) which could be caused by both different arrangement of O and U atoms in these configurations and sensitivity of uranium states to the presence of oxygen, thus indicating once more a strong oxygen chemical bonding (chemisorption). When oxygen molecule is located atop the surface U ion (the configuration 3), the U 5f and 6d contributions in the energy range above $-1 eV$ are diminished, simultaneously the O 2p contribution grows, thus increasing an overlap between all three states and indicating UO_2 quasi-molecular bond formation. As compared to the adsorption of oxygen molecule upon the hollow site (Fig. 3a), we again observe a higher O 2p peak

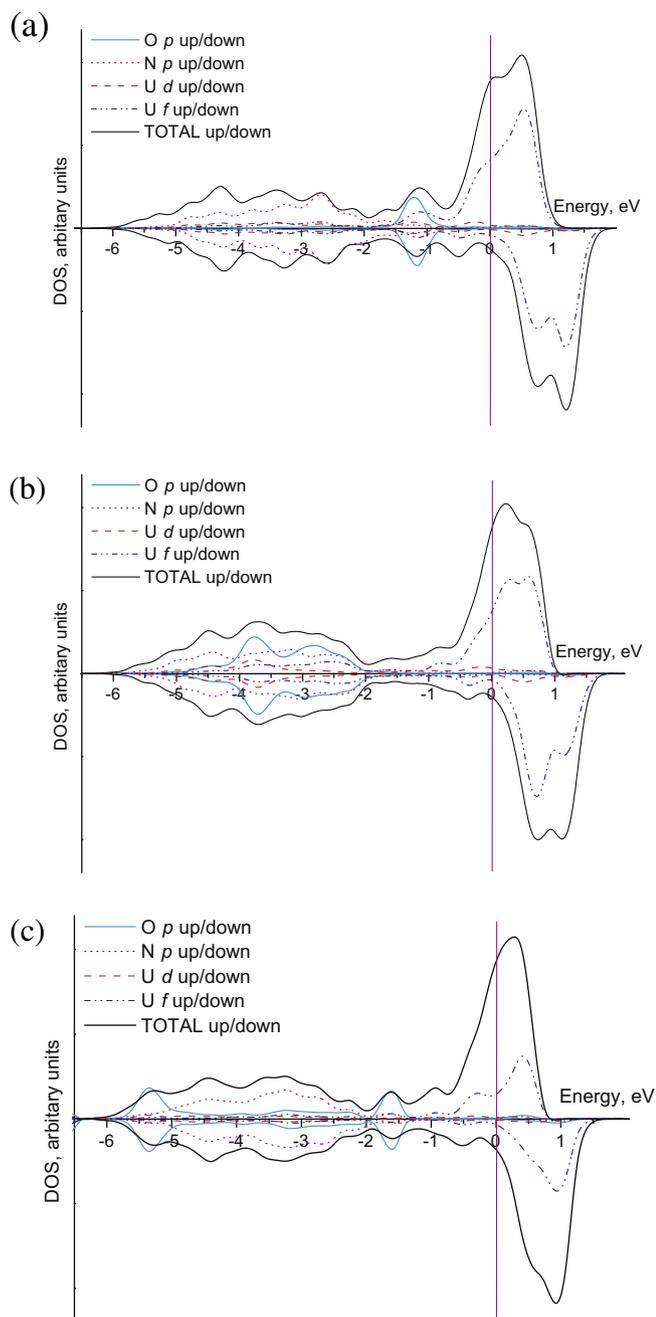


Fig. 3. The total and projected densities of states for three configurations of O_2 molecule as in Fig. 2 (the same a, b and c). The orbital projections of both O atoms as well as the nearest N and U ions are shown. The highest peaks have been normalized to the same value, whereas a convolution of individual energy levels has been plotted using the Gaussian functions with a half-width of 0.2 eV.

(at -1.5 eV) and an additional lower peak of the same O $2p$ (at -5.5 eV) which noticeably overlaps with the U $5f$ and $6d$ subpeaks (Fig. 3c). Similarity with the latter pattern was observed earlier for the projected DOS of O atom substituted for N in UN bulk [15]. In all three DOS (Fig. 3), a broad band corresponding to the N $2p$

projected states does not change drastically which means a weak effect of N ions on the O_2 molecule adsorption on the UN(0 0 1) surface.

4. Conclusions

Summing up, the results of our *ab initio* calculations clearly demonstrate a real possibility for spontaneous dissociation of the adsorbed oxygen molecules upon the perfect UN(0 0 1) surface, analogously to the O_2 dissociation on “traditional” metallic surfaces. This is the important step in understanding the initial stage of the UN oxidation mechanism.

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