## A Density Functional Study of Atomic Carbon Adsorption on $\delta$ -Pu(111) Surface

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Adsorption of atomic carbon on  $\delta$ -Pu(111) surface is investigated systematically using density functional theory with RPBE functional. The adsorption energies, adsorption structures, Mulliken population, work functions, layer and projected density of states are calculated in wide ranges of coverage, which have never been studied before as far as we know. It is found that the hcp-hollow sites is the energetically favorable site for all the coverage range considered. The repulsive interaction is identified, and the adsorption energy decreases with the coverage, while work function increases linearly with the coverage. It is found that the C-Pu interaction is very strong due to the hybridization between the C 2p states and the Pu 5f, Pu 6p,Pu 6d states of topmost layer Plutonium atoms.

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Plutonium metal is an important nuclear material widely used in the field of nuclear energy, weapon and out space. Plutonium is a reactive metal. When exposed to air, moisture, and common elements such as oxygen and hydrogen, the metal surface readily corrodes and forms a powder of small plutonium-containing particles.<sup>[1,2]</sup> Thus it has received considerable attention in order to understand the surface chemistry behavior and corrosion mechanism to ensure nuclear security. DFT method has been proved to be a powerful tool which can provide great insight in predicting properties of atomic and molecular adsorption on metallic surfaces.<sup>[3,4]</sup> In recent years, a number of DFT studies have been carried out to explore the electronic and geometric structures and related properties of surfaces to high accuracy, such as the adsorption behaviors of H, H<sub>2</sub>, O, O<sub>2</sub> and CO on  $\delta$ -Pu surface.<sup>[5-9]</sup> Previous experimental results indicate that the plutonium metal has resistance to further oxidation corrosion in the atmosphere of CO.<sup>[10]</sup> However, the anti-corrosion mechanism is still not clear in detail. The preliminary studies<sup>[11]</sup> suggest the dissociated adsorption of CO on plutonium metal surface with dissociated C and O atoms. Thus a layer of  $PuC_xO_y$  compound can be formed to resist the further corrosion. Our previous DFT calculations support this point of view.<sup>[13]</sup> There are no other more theoretical studies in the literature on carbon adsorption on the Pu surface. In fact, there are great controversies and significant discrepancies existing between various levels and types of theories calculation of molecular/atom adsorption on Pu surface. Thus using different methods, models and exchange and correlation functionals to investigate these problems thoroughly is necessary.

In this Letter, DFT calculations are performed with the program package DMol<sup>3</sup> in Materials Studio (version 4.0) of Accelrys Inc.,<sup>[14,15]</sup> employing the revised Perdew–Burke–Erzernhof (RPBE)<sup>[16]</sup> exchangecorrelation functional in the generalized gradient approximation (GGA).<sup>[17,18]</sup> For the C atom, a double numerical basis set with polarization functions  $(DNP)^{[19]}$  and a real space cut-off of 5.1 Å is used.<sup>[16]</sup> For Pu, the outer sixteen electrons  $(6s^26p^65f^67s^2)$ are treated as valence electrons and the remaining seventy-eight electrons are treated as core. A hardness conserving semi-local pseudopotential, called the density functional semi-core pseudo-potential (DSPP), has been used. A  $6 \times 6 \times 1$  Monkhorst-Pack<sup>[21]</sup> kpoint sampling is employed. The calculation method and parameters have been confirmed to characterize the atom/molecule adsorption on  $\delta$ -Pu surface in previous works.<sup>[13,22]</sup> The periodic boundary condition is used in the calculation with the repeated slab model. Here  $p(3 \times 3)$ ,  $p(2 \times 2)$ ,  $(\sqrt{3} \times \sqrt{3})R30^\circ$ ,  $p(1 \times 1)$  surface unit cells with a slab of three layers' thickness are chosen to model adsorption of  $\delta$ -Pu(111). In every case, a vacuum layer of 30 Å is added to the unit cell. The coverages of carbon atoms ( $\theta$ ) are 0.11 ML, 0.25 ML, 0.33 ML, 0.5 ML, 0.66 ML, 0.75 ML and 1.0 ML (monolayer) (Fig. 1). The carbon atoms are allowed to approach the Pu surface along four different symmetrical positions: Top position (T), Bridge position (B), Hcp hollow position (Hcp), Fcc hollow position (Fcc).



**Fig. 1.** Surface cells used in the calculations (top view) (Big balls represents the Pu atoms, small balls represent the C atoms).

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The average energy per C atom is defined as

$$E_{\rm ads} = -\frac{1}{N} (E_{\rm C/Pu(111)} - E_{\rm Pu(111)} - NE_{\rm C}).$$
(1)

With this definition,  $E_{ads}$  is positive when adsorption gives stabilization and reflects the relative stability of the adsorbate/substrate system.<sup>[23]</sup> The adsorption energies and the corresponding geometric parameters at possible adsorption sites are listed in Table 1.

We first comment on the carbon adsorption energy on  $\delta$ -Pu (111) surface for the same coverage. For the wide ranges coverage, from 0.11ML to 1.0 ML, adsorption energies are more than 4.4 eV, indicating that the interaction is chemical adsorption. Adsorption energies changes follow the order  $E_{\rm ads}({\rm Hcp}) \approx$  $E_{\rm ads}(Fcc) > E_{\rm ads}(B) > E_{\rm ads}(T)$ . This means that Hcp and Fcc sites, the most symmetrical sites, are the most favorable chemisorption sites with adsorption energies about  $5.5 \,\mathrm{eV}$ . For the Hcp and Fcc positions, the distances of the carbon atoms from the top layer have the lowest values of 1.45–1.51 Å with the three Pu atoms at the corners of the equilateral triangle being 2.38–2.42 Å apart. For the next most stable bridge position, the distances of the carbon atoms from the surface are about 1.66–1.68 Å, and the C-Pu distances are about 2.34–2.42 Å. For the top position, the distances of the carbon atoms from the surface and from Pu atom are nearest with the same value of about 2.28–2.37 Å. We note that the two hollow sites, only with the different arrangements of the secondand third-layer atoms, have just the same result of adsorption energy and geometry structure. Thus we can conclude that the adsorption of Pu with C mainly takes place in the first layer and the other two layers are only slightly affected. In view of the optimum distance versus chemisorption energy, it is evident that the number of Pu atoms which have action with C atom plays a significant role in the chemical bonding process.

Then we discuss the influences of the coverage of C atoms on adsorption energies and structures. From Fig. 2(a) and Table 1, it can be seen that the adsorption energy increases with the decreasing coverage  $\theta$ , meanwhile distance between C and surface  $(d_{\rm C-Pu})$ and the Pu-C bond length  $(r_{\rm C-P})$  decreases. These varies are almost linear with the coverage. In addition, when the coverage decreases to  $0.33 \,\mathrm{ML}$ , the adsorption energy increases to the max values 5.96 and 5.67 eV for Hcp and Fcc sites, respectively. This behavior is mostly due to the minimum repulsive interaction among the adsorbed C atoms at this coverage. Consequently the calculated adsorption energy for this configuration should represent a close estimation of the actual adsorption energy. This is similar to the adsorption behavior on transition metal surfaces with hexagonal close-packed structure.<sup>[25]</sup>

Table 1. Chemisorption energies, geometric structures and Mulliken population of C atom on  $\delta$ -Pu(111) surfaces for different positions. Here  $d_{C-Pu}$  is the distance between adsorption sites and the first layer,  $r_{C-Pu}$  is the Pu-H bond length,  $\Phi$  is the work function,  $\Delta \Phi$  is the work function change.

θ	Sites	$E_{\rm ads}$ (eV)	$d_{\rm C-Pu}$ (Å)	$r_{\rm C-Pu}$ (Å)	$\Phi$ (eV)	$\Delta \Phi$ (eV)	Mulliken charge				
							$q_{c(a.u.)}$	$q_{1\mathrm{st}}$	layer Pu(a.	u.)	
0.11	$\operatorname{top}$	4.712	2.288	2.288	4.949	0.197	-0.080	-0.254	-0.052	-0.051	-0.052
	Bridge	5.350	1.691	2.360	4.873	0.157	-0.179	-0.013	-0.027	-0.107	-0.106
	hcp	5.625	1.512	2.422	4.820	0.118	-0.195	-0.052	-0.075	-0.052	-0.051
0.25	fcc	5.596	1.515	2.426	4.820	0.116	-0.230	-0.045	-0.045	-0.060	-0.045
	$\operatorname{top}$	4.701	2.285	2.285	4.969	0.367	-0.082	-0.254	-0.052	-0.051	-0.052
	Bridge	5.367	1.690	2.355	4.885	0.283	-0.180	-0.013	-0.027	-0.107	-0.106
	hcp	5.612	1.507	2.419	4.843	0.241	-0.196	-0.052	-0.075	-0.052	-0.051
	fcc	5.586	1.512	2.423	4.846	0.244	-0.232	-0.045	-0.045	-0.060	-0.045
0.33	top	4.748	2.299	2.299	5.225	0.553	-0.128	-0.019	-0.211	-0.019	
	Bridge	5.431	1.682	2.349	5.129	0.457	-0.160	0.090	-0.122	-0.123	
	hcp	5.685	1.500	2.416	5.081	0.409	-0.168	-0.045	-0.044	-0.044	
	fcc	5.656	1.504	2.416	5.083	0.411	-0.209	-0.030	-0.030	-0.031	
0.50	top	4.624	2.325	2.324	5.315	0.715	-0.062	0.012	-0.175	0.012	-0.175
	Bridge	5.304	1.684	2.350	5.248	0.648	-0.091	-0.034	-0.04	-0.034	-0.04
	hcp	5.569	1.478	2.396	5.187	0.587	-0.126	-0.004	0.006	-0.004	0.006
	fcc	5.546	1.478	2.395	5.190	0.590	-0.160	-0.004	0.006	-0.004	0.006
0.66	top	4.564	2.336	2.336	5.480	0.808	-0.032	0.060	-0.152	-0.152	
	Bridge	5.237	1.686	2.352	5.402	0.730	-0.064	-0.196	0.200	0.290	
	hcp	5.515	1.467	2.396	5.400	0.728	-0.089	0.001	0.003	0.004	
	fcc	5.492	1.466	2.395	5.401	0.729	-0.124	0.030	0.030	0.030	
0.75	top	4.519	2.344	2.344	5.464	0.862	-0.025	0.062	-0.185	-0.185	-0.186
	Bridge	5.209	1.666	2.338	5.456	0.854	-0.025	0.037	0.038	-0.075	-0.085
	hcp	5.473	1.460	2.394	5.413	0.811	-0.072	0.011	0.011	-0.012	0.012
	fcc	5.451	1.460	2.393	5.414	0.812	-0.105	0.047	0.020	0.047	0.048
1.00	top	4.440	2.373	2.373	5.568	0.968	-0.020	-0.099	-0.099		
	Bridge	5.117	1.677	2.345	5.529	0.929	-0.026	-0.121	-0.121		
	hcp	5.378	1.451	2.387	5.599	0.999	-0.062	0.014	0.014		
	fcc	5.361	1.449	2.381	5.602	1.002	-0.092	0.056	0.056		

We also tabulate the change in work functions due to the C adsorption in Table 1. There are no experimental data of pure Pu surface work function. The reported calculation value of pure Pu surface varies from 4 eV to 5 eV. Our work is very closed to the work of Li *et al.*<sup>[9]</sup> Considering the unlikeliness of method, model and exchange-correlation potential etc. used in calculation, these differences are reasonable. In every case, C-chemisorbed Pu surface has higher work function than pure Pu surface. The increase in the work function is minimum for the Hcp and Fcc hollow positions and highest for the top position. As shown in Fig. 2(b), work function change  $\Delta \Phi$  is nearly linearly related to  $\theta$ .  $\Delta \Phi$  increases with  $\theta$ , which is similar to the fcc structure transition metal surface adsorption behavior. The following charge population analysis indicates that there are a few electron charges transferring from metal surface to the adsorbed C atom. With the coverage increasing, the transfer charges correspondingly increase, resulting in loss of surface electrons becomes more difficult. Accordingly, the work function and work function change also increase accordingly. The electrons transferring between surface and adsorbed C atoms form the dipole moment  $\mu$ . We use the Helmholtz equation<sup>[24]</sup> to calculate those  $\mu$  values,

## $\mu = (12\pi)^{-1} A \Delta \Phi / \theta,$

where A in units of Å<sup>2</sup> is the surface area of the  $p(1 \times 1)$  super-cell surface area. The relationship between  $\mu$  and  $\theta$  is shown in Fig. 2(c). The dipole moment increases with decreasing  $\theta$ . This is due to the fact that  $\mu$  is related to the charge transfer of each C atom. With the increase in coverage, electronic transfer from Pu to C becomes difficult accordingly, leading to average charge of the C atom to reduce. Thus the dipole moment is correspondingly reduced. This is the so-called depolarization effect. As can be seen from Fig. 2(c), when  $\theta$  is less than 0.33 ML, there is a leap variety of  $\mu$ . This is mostly because interaction among the adsorbed C atoms nearly reaches the minimum in low coverage ( $\theta < 0.33$  ML).

Mulliken population analysis is used to reveal the charge transferring after C atom adsorption. For bare Pu layers, the first and the third layers are negatively charged and the middle layer is positively charged. The charge of 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> layer Pu atoms are -0.148, 0.297 and -0.149, respectively. As shown in Table 1, when the adatom approaches, it gains electronic charge at the expense of the first layer, leaving the other two layers only slightly modified. For the Fcc site the C atom gains more negative charge compared to the other sites, followed by the Hcp, Bridge, and Top sites. This indicates that the ionic nature of the bond is stronger for the Fcc site. We also note that for the top site, the Pu atom directly below the carbon is negatively charged and the surrounding Pu atoms are positively charged. When  $\theta$  drops from 1.0

to 0.33 ML, the negative charges of adsorbed C atoms increase. For the Fcc site, the values are -0.092 to -0.209. When  $\theta$  is less than 0.33 ML, the negative charge of adsorbed C atoms is not more augmented. For all the cases, the first layers are positively charged, and the lower two layers are negatively charged. The charges of the first layers are significantly modified by the presence of the carbon atom, whereas the effects on the second and third layers are not strong. This fact is consistent in our anterior conclusion that the chemisorption activities mainly take place on the first layer.<sup>[7,13]</sup>



Fig. 2. The adsorption energies  $E_{ads}$  (a), work function changes  $\Delta \Phi$  (b) and dipole moments  $\mu$  (c) for carbon atom adsorbed on  $\delta$ -Pu(111) surface in different coverage.



Fig. 3. Difference charge density distributions for C chemisorbed on the  $\delta$ -Pu(111) surface ( $\theta = 0.75$  ML, Hcp site).

In Fig. 3, the difference charge density distributions for C adsorptions are shown for the Hcp site. We clearly see the charge accumulation around each adatom and the significant charge loss around the Pu atoms bonded to the adatoms, implying that the bond has a strong ionic character. The difference charge density plots are fairly consistent with the charges population shown in Table 1.

DOS analysis can provide fundamental understanding of the adsorbate-substrate interaction. Here we focus on analyzing the atomic partial density of states (PDOS) and layer-projected density of states (LDOS) for the most stable adsorption geometry (Hcp site), which allows us to establish which Pu and C atoms orbital contribute to the adsorbate-substrate hybrid states localized at the interface. Figure 4 shows the LDOS in successive layers, going from the surface towards the third layer for the most stable geometry. It seems that the topmost surface layer LDOS differs significantly from LDOS of the clean surface. An additional large peak appears in the energy region of  $-8.8 \,\mathrm{eV}$  to  $-8.0 \,\mathrm{eV}$ . For the subsurface layer, we note that the LDOS are slightly affected by the adsorbed C atoms. A peak with a bandwidth of 0.5 eV appears at energy ranges of  $-8.5 \,\mathrm{eV}$  to  $-8.0 \,\mathrm{eV}$ . While the third shows the character similar to that of the clean surface. Thus the interactions take place mainly between the topmost surface atoms and the adsorbed atoms. This is consistent with the fact that under the Fermi level, the surface layer LDOS shifts towards low energy compared with that of the clean surface, while the LDOS of the subsurface and third surface layers move upwards in energy. The adsorption of the C on  $\delta$ -Pu(111) surface is one exothermic reaction and the interactions between the adsorbed C atoms and the surface layer results in the surface layer LDOS shifts towards low energy, whereas the subsurface and third layers are slightly established by the adsorbed atoms.



Fig. 4. Layer-projected density of states (LDOS) for C on the Hcp site of  $\delta$ -Pu(111) surface ( $\theta = 0.75$  ML). In each case the solid and dotted lines denote for C on  $\delta$ -Pu(111) surface and clear  $\delta$ -Pu(111) surface, respectively: (a) for topmost surface, (b) for subsurface, (c) for the third layer.

To further analyze the interaction of the C atom with  $\delta$ -Pu (111) surface, we have calculated the PDOS of adsorbed C and the topmost surface atoms between the energy range from -10 to 5 eV relative to the Fermi level, as shown in Fig. 5. It can be seen that there is small hybridization between the C 2p states and Pu 5f, 6p, 6d states in the energy region of -8.6 eV to -8.0 eV. On the other hand, the valence bands are mostly from the surface C 2p states and Pu 5f, 6p, 6d states between the wide energy ranges from -4.5 to 0 eV. This indicates that the bonding between the carbon and the plutonium surface is mainly caused by hybridization between the C 2p states and Pu 5f, 6p, 6d states.



Fig. 5. Partial density of states (PDOS) for C adsorption on the Hcp site of  $\delta$ -Pu(111) surface ( $\theta = 0.75$  ML): (a) C atoms, (b) topmost layer Pu atoms.

In conclusion, we have investigated the adsorption of C atoms on  $\delta$ -Pu(111) surface by the DFT calculation in wide range coverage. The calculated results reveal that the most symmetrical Hcp and Fcp positions are the most stable configuration and the adsorption energies (about 5.6 eV) are quite large. Carbon atoms adsorb strongly on the surface. There is predominantly chemical bonding between C and the first layer Pu. Work functions, in general, tend to increase due to the presence of C adatom.

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