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A density functional study of carbon monoxide adsorption on (1 0 0) surface of γ-uranium

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Abstract

Adsorption of carbon monoxide on γ-U(1 0 0) surface has been studied at both non-spin-polarized and spin-polarized levels using the generalized gradient approximation of density functional theory (GGA-DFT) with Perdew and Wang (PW) functionals. For CO adsorption, the bridge position of (1 0 0) surface with Vert2 approach is found to be the most favorable site with a chemisorption energy of 2.9315 eV for the non-spin-polarized case, and 3.1875 eV for the spin-polarized case. The distances of the lower carbon atom from the uranium surface are found to be 1.589 Å and 1.716 Å for non-spin-polarized and spin-polarized cases, respectively. The distances between the carbon and oxygen atoms for this most favorable position are found to be 1.134 Å and 1.208 Å for the non-spin-polarized and spin-polarized cases, respectively. The magnetic moment for the most favorable site is found to be $0.042\mu_B$ per atom. A significant charge transfer from the first layer of the uranium surface to the carbon and oxygen atoms is found to occur, implying that the bonding is partly ionic. CO 2p orbitals are found to hybridize with U 5f bands resulting in more localization of the U 5f electrons. Spin polarization does increase the chemisorption energies by a small factor but does not play a significant role in the overall chemisorption process. Overall pattern of the density of states does not change significantly after the adsorption of CO on uranium layers. Also, in *none* of the cases studied, dissociation of CO molecule was possible for any of the approaches in any of the sites at the non-spin-polarized and spin-polarized levels of theory. This appears to contradict experimental results where CO adsorbed dissociatively on U surface. However, experimental data is for polycrystalline α-U at finite temperatures, whereas our present *ab initio* study refers to γ-U at 0 K.

Keywords: Actinides; Uranium; Adsorption; Density functional theory; Generalized gradient approximation

1. Introduction

Considerable theoretical efforts have been devoted to studying the electronic and geometric structures and related properties of surfaces to high accuracy in recent years. Actinides, as a group of strongly correlated and heavy fermion systems, especially have received notable increasing interests [1–4]. As is known, experimental work on actinides is relatively difficult to perform due to material problems and toxicity. On the other hand, they play important roles in advanced nuclear fuel cycles. Hence, theoretical studies are crucial for these high-Z elements. Such studies may also lead to a better understanding of the detailed surface corrosion mechanisms in the presence of environmental gases and thus help to address the environmental consequences of nuclear materials.

Uranium (U), the heaviest naturally occurring actinide element, is largely known due to its use as a nuclear reactor fuel. U occupies a central position in the early actinide series, with only three 5f electrons hybridizing with the 6d and 7s electrons showing itinerant behavior. Uranium crystallizes in to a rather open structure, the orthorhombic α-phase with four molecules per unit cell at ambient conditions, followed by the body-centered tetragonal β (bct) phase at 940 K and then the γ (bcc) phase at 1050 K at ambient pressure [5]. Moreover, the high temperature γ-phase can be studied at normal temperatures by the addition of certain metals like molybdenum, which stabilizes the γ-phase at room temperature and below [6]. It is found that in the field induced magnetic state, uranium metal has the spin and orbital moments ordered parallel, in contradiction to Hund's third rule and in sharp contrast to the free atom [7]. In fact, uranium could be the first example of a metal that becomes superconducting only under pressure without undergoing a crystallographic transition [8]. It was found recently, using the d-orbital energy, electronegativity and metallic radius as alloying parameters, that

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γ-uranium has a tendency of forming alloys with 3d transition metals [9]. These different aspects of the electronic bonding and structures in bulk uranium are bound to be enhanced at a surface or in a thin film of uranium adsorbed on a substrate, due to the reduced atomic coordination of the surface atoms and the narrow bandwidth of the surface states. Due to these reasons, adsorption of different materials, as carbon, oxygen, hydrogen and others, on the uranium surfaces and films can provide invaluable data regarding the bonding in uranium.

Using film-linearized-muffin-tin-orbital method, surface electronic structure of γ-uranium with body-centered cubic structure has been calculated using a five-layer slab of (1 0 0) surface [10]. This indicated that surface enhancement of 5f localization is much stronger for uranium than for plutonium, which may have important consequences for surface reconstruction, chemisorption and other surface behavior. The phase diagram of uranium has been studied in detail and it is concluded that the γ-phase is induced by partial localization of the 5f electrons at high temperature and also the body-centered cubic structure has been found to be the ultimate phase of the light actinides at elevated pressures [11]. In sharp contrast to this, using X-ray and ultra violet photoelectron spectroscopy and auger electron spectroscopy, it was found that in cases of thin films, localization effects are strong in Pu films, whereas in U films only weak effects have been observed [12]. Due to the narrow bandwidth of the surface states, any transition from delocalized to localized behavior first takes place, probably, at the U surface, with *possible* relaxations and reconstructions. The uranium–oxygen system is one of the most complex metal oxide systems due to the high reactivity of uranium with oxygen and towards oxygen containing systems such as H_2O, CO_2, and CO. Auger electron spectroscopy, and second ion mass spectroscopy have been used by McLean et al. [13] to study O_2, CO, and CO_2, adsorptions on thorium(1 1 1) crystal face and on polycrystalline α-uranium. Only atomic carbon and oxygen were observed on uranium, carbon produced by the dissociation diffused into the bulk, whereas the oxygen remained on the surfaces, forming an oxide. Ultraviolet and X-ray photoelectron spectroscopy have been used to study CO adsorption on polycrystalline U, UNi_2 and UNi_5 by Gouder et al. [14]. At 73 K, both dissociative adsorption and molecular chemisorption were observed at low exposure. The degree of molecular chemisorption was found to increase with the Ni content of the surface; while on pure U, only dissociative initial adsorption was observed, on UNi_2 and UNi_5, chemisorbed CO was observed. In this work, we report on the first *ab initio* study of CO interaction with the (1 0 0) surface of γ-U.

2. Computational formalism and discussion of results

As in *some* of our previous works [15,16], computations for our present work have been performed at the spin restricted and unrestricted generalized gradient approximation (GGA) level to density functional theory (DFT) using the DMol3 suite of programs [17–20]. DMol3 uses numerical orbitals for the basis functions, where each function corresponds to an atomic orbital. The physical wave function is expanded in an accurate numerical basis set and fast convergent 3D integration is used to calculate the matrix elements occurring in the Ritz variational method. Double numerical basis sets with polarization functions (DNP) are used for carbon and oxygen with a real space cut-off of 5.0 Å. The sizes of these DNP basis sets are comparable to the 6-31G** basis set of Hehre et al. [21]. However, they are believed to be much more accurate than a Gaussian basis set of the same size. For uranium, the outer 14 electrons ($6s^2$ $6p^6$ $5f^3$ $6d^1$ $7s^2$) are treated as valence electrons and the remaining 78 electrons are treated as core. A hardness conserving semilocal pseudopotential, density functional semicore pseudopotential (DSSP) [19] was used. The density functional semicore pseudopotentials were generated by fitting all-electron relativistic DFT results. These norm conserving potentials have a non-local contribution for each channel up to $l = 2$, as well as a non-local contribution to account for higher channels. To simulate periodic boundary conditions, a vacuum layer of 30 Å was added to the unit cell of the layers. The *k*-point sampling was done using the Monkhorst–Pack scheme [22]. The maximum number of numerical integration mesh points available in DMol3 was chosen for our computations and the threshold of density matrix convergence was set to 10^{-6} and a smearing parameter of 0.005 Ha was used.

Although the uranium metal is believed to be paramagnetic, an ultrathin film (UTF) of uranium could be magnetic due to local magnetic ordering at the narrower electronic bands on the surface. Also, ^{235}U nuclear magnetic resonance in UO_2 was observed and it was predicted that UO_2 becomes a non-collinear anti-ferromagnet below 30.8 K [23]. Thus, to understand the influence of spin/magnetism on the chemisorption process, we performed both non-spin-polarized and spin-polarized calculations. As for the effects of relativity, DMol3 does not yet allow fully relativistic computations and as such, we have used the scalar-relativistic approach, as available in Dmol3. In this approach, the inclusion of spin–orbit coupling is omitted primarily for computational reasons but all other relativistic kinematic effects such as mass–velocity, Darwin, and higher order terms are retained. It has been shown [19] that this approach models actinide bond lengths fairly well. We certainly do not expect that the inclusion of the effects of spin–orbit coupling, though desirable, will alter the primary qualitative and quantitative conclusions of this paper, particularly since we are interested in chemisorption energies defined as the difference in total energies. All our calculations are done on a Compaq ES40 alpha multi-processor supercomputer at the University of Texas at Arlington.

To study carbon monoxide adsorption on the γ-uranium(1 0 0) surface, we modeled the surface with three layers of uranium at the experimental lattice constant of 3.467 Å. Due to severe demands on computational resources, we have not considered the possibilities of surface relaxations and reconstructions. We should note also that any relaxation is expected to be quite small. As an example, we did relax the surface monolayer. At the NSP level, the separation of the first and the second layers decreased by about 5%, with the total energy changing by 0.078 a.u. (less than 0.008%). At the SP level, on the other hand, the separation increased by about 5%, with the total energy changing by 0.088 a.u. (less than

0.009%). Since CO adsorption on a surface composed of heavy U atoms is not expected to change this minor relaxation and since chemisorption energy is defined as the difference in total energies, we do not believe that our approximation will, in any way, alter the primary qualitative and quantitative conclusions of this study. Also, we believe that this three-layer uranium slab is adequate considering that the oxygen and carbon atoms are not expected to interact with atoms beyond the first three layers. This has been found to be the case in our studies of oxygen and hydrogen atom adsorptions on the plutonium surface [24]. Also, recently, Ray et al. have shown in studies of quantum size effects of δ-plutonium and fcc americium surfaces that surface energies converge well within the first three layers [25]. Due to severe demands on computational resources, the unit cell per layer was chosen to contain four uranium atoms. Thus, our three-layer model of the surface contains 12 uranium atoms. The CO molecule, one per unit cell, was allowed to approach the uranium surface along three symmetrically distinguishable sites: (i) directly on top of a U atom (*top* position); (ii) on the middle of two nearest neighbor U atoms (*bridge* position); (iii) in the center of the smallest unit structures of the surfaces (*center* position). We also considered several interstitial positions and found that none of them gave a bound state with or without spin polarization. For each of these positions we considered several approaches of adsorption: (1) CO molecule approaches vertically to the surface with oxygen atom facing the surface (Vert1 approach); (2) CO molecule approaches vertically to the surface with carbon atom facing the surface (Vert2 approach); (3) CO molecule parallel to the surface and parallel to the bcc lattice vectors (Hor1 approach); (4) CO molecule parallel to the surface having an angle of 45° with the bcc lattice vectors, i.e., parallel to the diagonal of the square lattice (Hor2 approach). For the case of Hor1 and Hor2 approaches, due to periodic boundary conditions, we did not change the direction of CO molecule as it is parallel to the surface and interacts with the neighboring atoms equally. Also for both the horizontal approaches the carbon and the oxygen atoms of the CO molecule are at the same distance from the uranium surface, whereas for the vertical approach one of either carbon or oxygen atom is closer to the surface than the other. The adsorption energy is then calculated from

$$E_c = E(\text{U-layers}) + E(\text{CO}) - E(\text{U-layers} + \text{CO})$$

For the non-spin-polarized case, both E(U-layers) and E(U-layers + CO) were calculated without spin polarization, while for spin-polarized calculations, both of these two energies are spin-polarized. E(CO) is the energy of the carbon monoxide molecule in the ground state for both the non-spin-polarized and the spin-polarized cases. The optimized adsorption energies, and the corresponding optimized distances, are given in Tables 1 and 2 for the non-spin-polarized and spin-polarized cases, respectively. The distances r_d given in the table are measured as the distance from the uranium surface to the oxygen or carbon atom, if both the atoms are at same height, or to the nearer oxygen or carbon atom if one of them is closer to the surface than the other; r_o is the optimized distance between the C and the O atoms for the CO molecule.

Table 1

Chemisorption energies (CE) in eV for different sites and approaches with adsorption distances r_d in Å from the uranium surface and C–O distances, r_o in Å for the non-spin-polarized case

Sites	Approach	r_d (Å)	r_o (Å)	CE (eV)
Top	Vert1	2.817	1.146	0.9148
	Vert2	2.342	1.139	2.7037
	Hor1	2.611	1.335	1.6548
	Hor2	2.785	1.310	2.9306
Bridge	Vert1	2.670	1.129	1.1036
	Vert2	1.589	1.134	2.9315
	Hor1	1.782	1.357	2.1765
	Hor2	1.989	1.411	1.7505
Center	Vert1	0.789	1.142	1.1914
	Vert2	0.613	1.311	2.9298
	Hor1	0.711	1.319	2.7599
	Hor2	0.774	1.427	2.5439

For all the approaches r_d is calculated from the lower oxygen or carbon atom to the uranium surfaces. There are four approaches—(i) CO molecule approaches vertically to the surface with O on the lower end, Vert1; (ii) CO molecule approaches vertically to the surface with C on the lower end, Vert2; (iii) CO molecule parallel to the surface and parallel to the bcc lattice vectors, Hor1; (iv) CO molecule parallel to the surface and having an angle 45° with the bcc lattice vectors, Hor2.

We start by describing the chemisorption process of CO at different sites on the uranium surface. Consider first the top sites without spin polarization (Table 1 and Fig. 1). As mentioned before, there are four different approaches for each site. For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 2.817 Å and 2.342 Å; while the chemisorption energies are 0.9148 eV and 2.7037 eV, respectively. In the Vert1 and Vert2 approaches, the distance between the carbon and oxygen atoms (r_o) is 1.146 Å and 1.139 Å, respectively, which implies that dissociation of the CO molecule is not possible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances

Table 2

Chemisorption energies (CE) in eV for different sites and approaches with adsorption distances r_d in Å from the uranium surface and C–O distances, r_o in Å for the spin-polarized case and magnetic moments of CO chemisorbed uranium layers in μ_B per atom

Sites	Approach	r_d (Å)	r_o (Å)	CE (eV)	Magnetic moments (μ_B/atom)
Top	Vert1	2.845	1.211	1.9734	0.143
	Vert2	2.313	1.198	2.8812	0.038
	Hor1	2.732	1.348	1.8132	0.092
	Hor2	2.790	1.391	3.1781	0.085
Bridge	Vert1	2.619	1.188	1.2782	0.034
	Vert2	1.716	1.208	3.1875	0.042
	Hor1	1.811	1.381	2.3225	0.016
	Hor2	1.892	1.442	1.9278	0.131
Center	Vert1	0.764	1.217	1.3485	0.004
	Vert2	0.691	1.391	3.1672	0.189
	Hor1	0.754	1.438	2.9104	0.015
	Hor2	0.804	1.482	2.7111	0.029

For all the approaches r_d is calculated from the lower oxygen or carbon atom to the uranium surfaces.

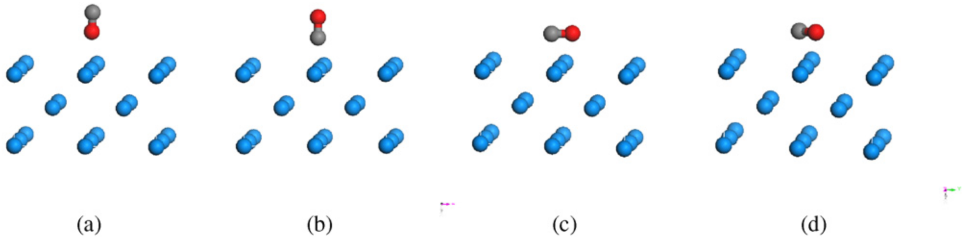


Fig. 1. CO adsorption on U(1 0 0) surface at top site with different approaches: (a) Vert1, (b) Vert2, (c) Hor1 and (d) Hor2.

(r_d) from the uranium surface to the CO molecule are 2.611 Å and 2.785 Å; while the chemisorption energies are 1.6548 eV and 2.9306 eV, respectively. In the Hor1 and Hor2 approaches, the distance between the carbon and oxygen atom (r_o) is 1.335 Å and 1.310 Å, respectively, which is stretched more compared to the Vert1 and Vert2 approaches, but not enough for them to be dissociated. This shows that dissociation of CO molecule is not possible for any of the approaches along the top site for the non-spin-polarized case.

Inclusion of spin polarization did not change the overall features of any of the approaches along the top site (Table 2 and Fig. 1). For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 2.845 Å and 2.313 Å; while the chemisorption energies are 1.9734 eV and 2.8812 eV, respectively. In the Vert1 and Vert2 approaches, the distance between the carbon and oxygen atom (r_o) is 1.211 Å and 1.198 Å, respectively, which implies that dissociation of CO molecule is not possible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 2.732 Å and 2.790 Å; while the chemisorption energies are 1.8132 eV and 3.1781 eV, respectively. In the Hor1 and Hor2 approaches, the distance between the carbon and oxygen atom (r_o) is 1.348 Å and 1.391 Å, respectively, which is stretched more compared to the Vert1 and Vert2 approaches, but not enough for them to be dissociated. The chemisorption energies and the distances between the carbon and oxygen atom and from the surface increases by a small factor compared to the non-spin-polarized case, but the overall picture does not change significantly for the spin-polarized case. Also for the top site, considering all the approaches for non-spin-polarized and spin-polarized cases, the Hor2 approach is found to be the most favorable while Vert1 is found to be least favorable.

For the bridge sites along the four different approaches (Table 1 and Fig. 2), we discuss first the results for the non-spin-polarized case. For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 2.670 Å and 1.589 Å; while the chemisorption energies are 1.1036 eV and 2.9315 eV, respectively. The distances between the carbon and oxygen atom (r_o) are 1.129 Å and 1.134 Å, respectively, which implies that dissociation of CO molecule is not possible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 1.782 Å and 1.989 Å; while the chemisorption energies are 2.1765 eV and 1.7505 eV, respectively. In the Hor1 and Hor2 approaches, the distances between the carbon and oxygen atom (r_o) are 1.357 Å and 1.411 Å, respectively, which is stretched more compared to the Vert1 and Vert2 approaches, but not enough for them to be dissociated. This shows that dissociation of CO molecule is not possible for any of the approaches along the bridge site for the non-spin-polarized case.

Similar to the case for the top site, inclusion of spin polarization did not change the overall features of any of the approaches along the bridge site (Table 2 and Fig. 2). For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 2.619 Å and 1.716 Å; while the chemisorption energies are 1.2782 eV and 3.1875 eV, respectively. The distances between the carbon and oxygen atom (r_o) are 1.188 Å and 1.208 Å, respectively, which implies that dissociation of CO molecule is not possible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 1.811 Å and 1.892 Å; while the chemisorption energies are 2.3225 eV and 1.9278 eV, respectively. In the Hor1 and Hor2 approaches, the distances between the carbon and oxygen atoms (r_o) are 1.381 Å and 1.442 Å, respectively, which is stretched more compared to the Vert1 and Vert2 approaches, but not enough for them to be dissociated. The chemisorption energies and the distances between the carbon and oxygen atom and from the surface increases by a small factor compared to the non-spin-polarized case, but the overall picture does not change significantly for the spin-polarized case. Also for the bridge site, considering all the approaches for non-spin-polarized and

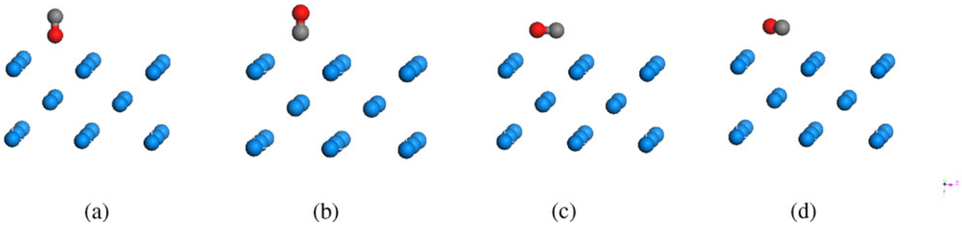
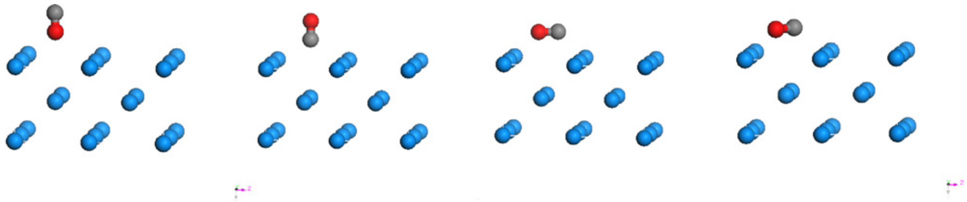


Fig. 2. CO adsorption on U(1 0 0) surface at bridge site with different approaches: (a) Vert1, (b) Vert2, (c) Hor1 and (d) Hor2.



(a) (b) (c) (d)

Fig. 3. CO adsorption on U(1 0 0) surface at center site with different approaches: (a) Vert1, (b) Vert2, (c) Hor1 and (d) Hor2.

spin-polarized cases, the Vert2 approach is found to be the most favorable while Vert1 is found to be least favorable.

Moving to the center sites along the four different approaches (Table 1 and Fig. 3), we discuss the results for the non-spin-polarized case. For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 0.789 Å and 0.613 Å; while the chemisorption energies are 1.1914 eV and 2.9298 eV, respectively. In the Vert1 and Vert2 approaches, the distances between the carbon and oxygen atoms (r_o) are 1.142 Å and 1.311 Å, respectively, which implies that dissociation of CO molecule is not possible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 0.711 Å and 0.774 Å; while the chemisorption energies are 2.7599 eV and 2.5439 eV, respectively. In the Hor1 and Hor2 approaches, the distances between the carbon and oxygen atoms (r_o) are 1.319 Å and 1.427 Å, respectively, which is stretched more compared to the Vert1 and Vert2 approaches, but not enough for them to be dissociated. This shows that dissociation of CO molecule is not possible for any of the approaches along the center site for the non-spin-polarized case.

Similar to the case for the top and bridge site, inclusion of spin polarization did not change the overall features of any of the approaches along the center site (Table 2 and Fig. 3). For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 0.764 Å and 0.691 Å; while the chemisorption energies are 1.3485 eV and 3.1672 eV, respectively. In the Vert1 and Vert2 approaches, the distances between the carbon and oxygen atoms (r_o) are 1.217 Å and 1.391 Å, respectively, which implies that dissociation of CO molecule is not possible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances (r_d) from the uranium surface to the CO molecule are 0.754 Å and 0.804 Å; while the chemisorption energies are 2.9104 eV and 2.7111 eV, respectively. In the Hor1 and Hor2 approaches, the distances between the carbon and oxygen atoms (r_o) are 1.438 Å and 1.482 Å, respectively, which is stretched more compared to the Vert1 and Vert2 approaches, but not enough for them to be dissociated. The chemisorption energies and the distances between the carbon and oxygen atom and from the surface increases significantly compared to the non-spin-polarized case, but the overall picture does not change significantly for the spin-polarized case. Also for the center site, considering all the approaches for non-spin-polarized and spin-polarized cases, the Vert2 approach in spin-polarized configuration is found to be the most favorable site while Vert1 in non-spin-polarized configuration is found to be least favorable, similar to the results obtained for the bridge site.

From the above discussions it is clear that the Vert1 approach where the O atom is at the lower end, is not preferred approach for any of the three sites. Basically in adsorptions at Vert1 and Vert2 approaches, either the oxygen or carbon atom is at the lower end and coordinated with the uranium surface, whereas the other atom is only coordinated with the other atom of the CO molecule. This shows why Vert1 approach is the least favorable, but on the same side the Vert2 approach is, in general, found to be favorable for all sites, except for the top site. This indicates that for the Vert2 approach where the carbon atom is at the lower end, the interaction of the carbon atom with the uranium atoms is very strong. For Vert1 approach, we have significantly lower chemisorption energies and the distances between the CO molecule and the uranium surface is higher compared to other approaches. Also usually all the approaches along the center site are seen to be more preferred compared to the bridge and the top site except for Hor2 approach on top site and Vert2 approach on bridge site. This is due to the fact that in the center site the CO molecule is very close to the uranium surface, irrespective of the approach, and hence the uranium atoms interact with both the carbon and oxygen atoms. But considering all the approaches along all the sites, bridge site with Vert2 approach is found to be the most favorable for both non-spin-polarized and spin-polarized configurations. Also, in *none* of the cases studied, dissociation of CO molecule was found to be possible for any of the approaches in any of the sites at the non-spin-polarized and spin-polarized levels of theory. This appears to contradict experimental results [13,14] where CO adsorbed dissociatively on U surface. However, we hasten to point out that experimental data is for polycrystalline α-U at finite temperatures, whereas our present *ab initio* study refers to γ-U at 0 K. Experimental results on γ-U and theoretical studies on α-U would be very welcome.

We also performed Mulliken spin and charge distribution [26] for the most stable chemisorption site in the spin-polarized case, namely, the bridge site at the Vert2 approach. Both the oxygen and carbon atoms acquire negative charges, −0.185 and −0.033, respectively, primarily from the first layer of uranium atoms, with the first layer being positively charged as a result. Thus, there exists an ionic part in the U–CO bonding, along with other contributions. The oxygen and carbon atoms acquire negative spins of −0.056 and −0.083, basically from the top layer of uranium atoms. The spins in the first and second layer are seen to be affected by the chemisorption of CO molecule, with all but one atom having positive spins compared to the bare uranium layers. The third layer seems to be least affected by the chemisorption process, showing the tendency of CO molecule to interact more with the top two layers of uranium. In fact, our detailed study indicates that in all cases the CO molecule interacts primarily with the first two layers of uranium atoms, with the third layer being only slightly affected and the first layer significantly affected.

Table 2 also shows the magnetic moments of the CO adsorbed uranium layers for different adsorption configurations. The magnetic moments of the bare uranium layers drop rapidly as the number of layers increase, from $4.345\mu_B$ for the monolayer to $1.610\mu_B$ for the three-layer. This indicates that the semi-infinite uranium metal surface might be paramagnetic. We note that our value for the magnetic moment of three layers of uranium slab is higher that the spin magnetic moment of $0.84\mu_B$ per atom for α-uranium predicted by Stojic et al. [27] using the full-potential-linearized-augmented-plane-wave (FPLAPW) method in the generalized gradient approximation. Most of the magnetic moments tabulated in Table 2 are of very low value, and lack any specific orderings. It can be seen that all of the CO chemisorbed layers are basically paramagnetic. The most favorable chemisorption configuration, bridge site with Vert2 approach, has a magnetic moment of $0.042\mu_B$ per atom. The highest magnetic moment of $0.189\mu_B$ per atom is found for center site with Vert2 approach. We note that the non-spin-polarized chemisorption energies for different cases studied is, in general, smaller than the spin-polarized chemisorption energies but the overall trends remain the same. We conclude that spin-polarization does not play a significant role in the CO on U chemisorption process.

From the band energetic of the bare and CO adsorbed uranium layers, we also found that the change in band gaps due to the inclusion of spin polarization is very small. For instance, the energy gaps for uranium 6p and 5f bands without spin polarization is 14.806 eV compared to 14.436 eV with spin polarization. For the CO adsorbed layers (considering only the most favored chemisorption configuration, bridge site with Vert2 approach) these values are 6.654 eV and 7.268 eV, respectively. It can be seen that the non-spin-polarized energy gaps for bare uranium layers are higher that the spin-polarized which is exactly opposite for the case of CO adsorbed layers. It can be inferred from these energies that the adsorption of CO reduces the gaps. This is due to fact that the oxygen and carbon 2p orbitals hybridize with the lower end of uranium 5f orbitals and split the 5f band. There exists a small band gap of 2.591 eV (3.012 eV with spin polarization) between the hybridized CO 2p and U 5f band and the remaining U 5f electrons. Also it was found that upon CO adsorption the lower part of the 5f band become more localized, whereas the upper part is always hybridized with uranium 6d and 7s electrons.

Density of states are plotted for the most stable adsorption configuration, bridge site with Vert2 approach, and com-

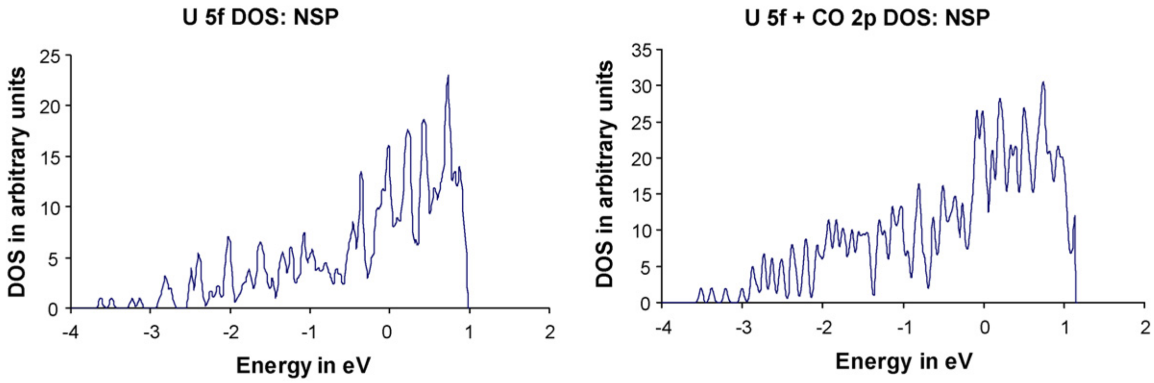

U 5f DOS: NSP
U 5f + CO 2p DOS: NSP

Fig. 4. Density of states for U 5f for the non-spin-polarized (NSP) case for bare uranium and non-spin-polarized (NSP) case for the center position, Vert2 approach. Fermi energy is normalized to zero.

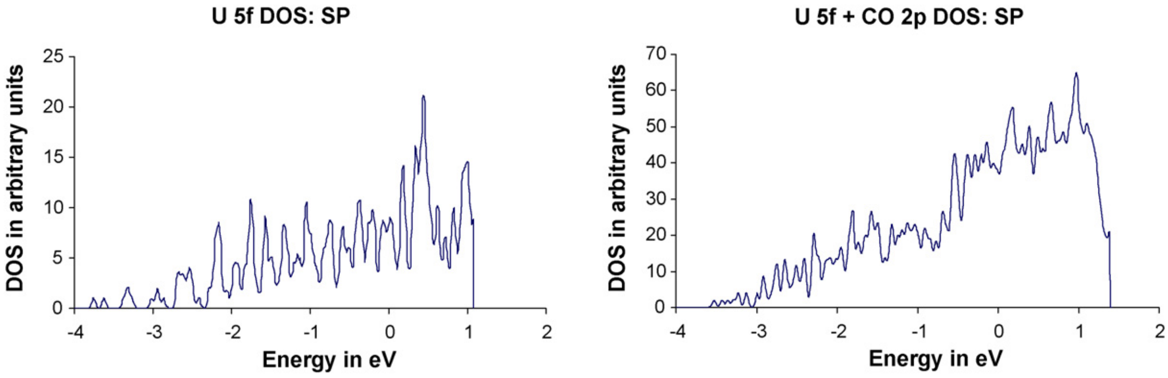

U 5f DOS: SP
U 5f + CO 2p DOS: SP

Fig. 5. Density of states for U 5f for the spin-polarized (SP) case for bare uranium and spin-polarized (SP) case for center position, Vert2 approach. Fermi energy is normalized to zero.

pared with the density of states for the bare uranium at the non-spin and spin-polarized level (Figs. 4 and 5). Comparing the bare uranium and CO adsorbed uranium layers, it was found that density of states increases for the CO adsorbed uranium layers, for both the non-spin and spin-polarized cases, but the overall pattern of the density of states does not change significantly.

3. Conclusions

In conclusion, the chemisorption of CO molecule on (1 0 0) surface of γ-uranium has been investigated using the generalized gradient approximation to density functional theory. In *none* of the cases studied, dissociation of CO molecule was possible for any of the approaches in any of the sites at the non-spin-polarized and spin-polarized levels of theory. This appears to contradict experimental results where CO adsorbed dissociatively on U surface. However, we hasten to point out that experimental data is for polycrystalline α-U at finite temperatures, whereas our present *ab initio* study refers to γ-U at 0 K. Experimental results on γ-U and theoretical studies on α-U thus would be very welcome. Molecular adsorption of CO is observed in all cases with bridge site with Vert2 approach being the most favorable. Interstitial adsorptions of molecular CO are less probable, as no bound states were observed. CO 2p orbitals are found to hybridize with U 5f bands, and a part of the U 5f electrons become more localized. A significant charge transfer from the first layer of the uranium surface to the carbon and oxygen atoms is found to occur, implying that the bonding is partly ionic. Though increasing the chemisorption energies by a small amount, spin polarization does not have considerable effect on the chemisorption process. Magnetic moments of different adsorption configurations suggest most of them to be paramagnetic.

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