ON THE BEHAVIOR OF 5f ELECTRONS

by

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ABSTRACT

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Considerable theoretical efforts have been devoted in recent years to studying the electronic and geometric structures and related properties of surfaces to high accuracy. One of the many motivations for this burgeoning effort has been a desire to understand the detailed mechanisms that lead to surface corrosion in the presence of environmental gases; a problem that is not only scientifically and technologically challenging but also environmentally important. Such efforts are particularly important for systems like the actinides for which experimental work is relatively difficult to perform due to material problems and toxicity. As is known, the actinides are characterized by a gradual filling of the *5f*-electron shell with the degree of localization increasing with the atomic number Z along the last series of the periodic table. The open shell of the *5f* electrons determines the magnetic and solid-state properties of the

actinide elements and their compounds and understanding the quantum mechanics of the 5f electrons with increasing prominence of relativistic effects is the defining issue in the physics and chemistry of the actinide elements. The 5f orbitals have properties intermediate between those of localized 4f and delocalized 3d orbitals and as such, the actinides constitute the "missing link" between the d transition elements and the lanthanides. Among the actinide elements, uranium is well known due its use as a nuclear reactor fuel and is the heaviest naturally occurring actinide element. It is located in the middle of the early part of the actinide series, with only three 5f electrons hybridizing with the 6d and 7s electrons and demonstrating itinerant behavior. The proportion of the outer shell s and d electrons is larger in uranium compared to plutonium and a study of the electronic structure of U can provide significant clues about the crossover from delocalized to localized 5f-electron behavior supposed to occur somewhere in the region of the periodic table from uranium (with 3 5f electrons) to plutonium (5 5f electrons) to americium (with 6 5f electrons). Uranium crystallizes in the orthorhombic α -phase with four molecules per unit cell at ambient condition, followed by the body-centered tetragonal β phase at 940 K and then the body-centered γ phase at 1050 K at ambient pressure. However, certain impurities like molybdenum can stabilize the γ -phase at room temperature or below. In this work, oxygen and carbon adsorptions on the (100) surface of γ -uranium have been studied at both non-spinpolarized and spin-polarized levels using the generalized gradient approximation of density functional theory (GGA-DFT) with Perdew and Wang (PW) functionals. For oxygen and carbon adsorption, various chemisorption sites such as, top, bridge, center,

and interstitial have been investigated. Details of energetics of the chemisorption process, such as chemisorption energies, adatom separation distances, spin and charge distributions, energy band gaps and density of states will be presented. Magnetic moments are also calculated for bare uranium and oxygen and carbon adsorbed system. The changes in the uranium surface after adsorption of oxygen and carbon are analyzed and compared with the adsorption of atomic oxygen adsorption on the plutonium (100) surface. Also adsorption of molecular carbon monoxide and possible dissociative adsorption on uranium surface will be presented at both non-spin-polarized and spin-polarized levels of theory. For adsorption of carbon monoxide, different approaches such as Vert1, Vert2, Hor1 and Hor2 are studied at top, center, and bridge chemisorption sites. The role of 5f electrons in the bonding of uranium with the oxygen and carbon adatom, and with the carbon monoxide molecule will be discussed.

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CHAPTER 1

INTRODUCTION

Considerable theoretical efforts have been devoted in recent years to studying the electronic and geometric structures and related properties of surfaces to high accuracy. One of the many motivations for this burgeoning effort has been a desire to understand the detailed mechanisms that lead to surface corrosion in the presence of environmental gases; a problem that is not only scientifically and technologically challenging but also environmentally important. Such efforts are particularly important for systems like the actinides for which experimental work is relatively difficult to perform due to material problems and toxicity. As is known, the actinides are characterized by a gradual filling of the 5f-electron shell with the degree of localization increasing with the atomic number Z along the last series of the periodic table. The open shell of the 5f electrons determines the magnetic and solid-state properties of the actinide elements and their compounds and understanding the quantum mechanics of the 5f electrons is the defining issue in the physics and chemistry of the actinide elements. These elements are also characterized by the increasing prominence of relativistic effects and their studies can, in fact, help us understand the role of relativity throughout the periodic table [1-3]. Narrower 5f bands near the Fermi level, compared to 4d and 5d bands in transition elements, are believed to be responsible for the exotic

structure of the actinides at ambient condition [4]. The 5f orbitals have properties intermediate between those of localized 4f and delocalized 3d orbitals and as such, the actinides constitute the "missing link" between the d transition elements and the lanthanides [5]. Thus, a proper and accurate understanding of the actinides will help us understand the behavior of the lanthanides and transition metals as well. The similarity between light actinides (Th – Pu) and the *d*- transition elements is due to the fact that both of them are supposed to have delocalized *f* and *d* electrons, respectively [6-7].

Uranium (U) is well known due its use as a nuclear reactor fuel and is the heaviest naturally occurring actinide element. It is located in the middle of the early part of the actinide series, with only three 5f electrons hybridizing with the 6d and 7s electrons and demonstrating itinerant behavior. The proportion of the outer shell s and d electrons is larger in uranium compared to plutonium and a study of the electronic structure of U can provide significant clues about the crossover from delocalized to localized 5f-electron behavior [8]. Uranium crystallizes in the orthorhombic α -phase with four molecules per unit cell at ambient condition, followed by the body-centered tetragonal β (bct) phase at 940 K and then the γ (bcc) phase at 1050 K at ambient pressure [9]. However, certain impurities like molybdenum can stabilize the γ -phase at room temperature or below [10]. The unfilled narrow 5f bands and the complexities in bonding in U might arise from the fact that U has valence shell which breaks Hund's third rule [11]. U also was one of the first examples of metal that undergoes superconducting transition under pressure without crystallographic transition [12]. Using d-orbital energy, electronegativity, and metallic radius as alloying parameters, Kurihara *et al.* observed that $\gamma - U$ has a tendency of forming alloys with 3*d* transition metals [13]. These unusual aspects of the electronic bonding and structures in bulk uranium are apt to be enhanced at a surface or in a thin layer of uranium adsorbed on a substrate, due to the reduced atomic coordination of a surface atom and the narrow bandwidth of the surface states. For this reason, uranium surfaces and films and adsorptions on such may provide a valuable source of information about the bonding in uranium. Hao *et al.* [8] in a study of a five layers slab of (100) γ -uranium surface using the film-linearized-muffin-tin-orbitals (FLMTO) method suggested that surface enhancement of 5f localization (relative to bulk) is much stronger for uranium than for plutonium, with important consequences for surface reconstruction, chemisorption, and other surface behavior. The phase diagram of uranium has been studied to 100 GPa by in situ diamond-anvil-cell x-ray/laser-heating experiments [14]. Based on their results and free energy calculations, the authors conjectured that the γ - phase is induced by partial localization of the 5f electrons at high temperatures. In contrast, using surface spectroscopic techniques such as XPS, UPS, and AES, Gouder [15] concluded that the localization effects are strong in Pu films, whereas in U films effects are weak. Considering the narrow bandwidth of the surface states, any transition from itinerant to localized behavior probably first takes place 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 U with O_2 and towards oxygen containing systems such as H₂O, CO and CO₂. We have provided a summary of the published literature on uranium-oxygen systems in our earlier work on molecular oxygen adsorption on (100) surface of γ – uranium [16]; however, for the sake of completeness, we repeat the status of the literature on uranium-oxygen and uranium-carbon systems to date below. A large number of oxide phases exist with a wide variety of stoichiometry [17]. Oxidation of metallic uranium surface has its technological importance primarily because of the atmospheric corrosion of uranium, and the formation of passivation layers protecting further corrosion attack [18-19]. At temperature below 35°C, the reaction of uranium with water is totally suppressed and $U+O_2$ becomes the preferred reactions [20]. McLean *et al.* [21] used x-ray photoelectron spectroscopy, Auger electron spectroscopy and second ion mass spectroscopy to study O₂, CO and CO₂ on thorium and uranium surfaces. They showed that the adsorbed molecules dissociate and the carbon defused in the bulk, whereas the oxygen remained on the surfaces forming an oxide. They also mentioned that the spectrum of uranium at saturation oxygen coverage closely resembles to that of UO₂. A similar study by Swissa and Bloch et al. [18] reached the same conclusion. On the study of the progression of U-O surface reaction, this group showed that the chemisorbed oxygen formed islands on the uranium surface, later spreading over the surface. Gouder *et al.* [22] used ultraviolet photo-spectroscopy to study the reaction of O₂ on uranium surface and showed that dissociative chemisorption of oxygen is followed by the formation of sub-stoichiometric UO2-x and hyperstoichiometric UO_{2+x} on the surface. They also found that O₂ adsorption results in a decrease of Fermi level emission and the increase of the U 5f² and O 2p emission, which means the withdrawal of the 5f electrons from the Fermi level and their transfer

into O 2p and the localized U $5f^2$ level. On the experimental side, the data on carbon interaction with uranium surface is relatively scarce. The passivation of uranium surfaces against air corrosion, by N_2^+ and C^+ ion implantation processed have been studied, using surface analysis methods. Thin modified surface layers with gradual gradients of the corresponding nitrides and carbides were produced. This avoided the formation of discontinuous interfaces typical to coatings [23]. Thin layers of UC_x (x =0-12) have been prepared by sputter co-deposition of uranium and carbon in an Ar atmosphere by Eckle et al [24]. The films were investigated in situ by ultraviolet and Xray photoelectron spectroscopy. A strong hybridization was found between C-2p and U-5f states for UC, while the C-2p in UC₂ signal was weakly hybridized, and for higher carbon contents a π – bond characteristic of graphite appeared. It was shown that analysis of the α -, β - and γ -phases of uranium by a hard sphere model based on a simple bond description leads to fractional packing densities q which agree with the missing primary solute solubilities of C, N and O in α - and β -U. [25] With the help of electron microscopy and electron diffraction, it was shown that uranium in thin film assumes the β -phase structure, which is tetragonal. [26] Using ultraviolet and X-ray photoelectron spectroscopies CO adsorption on uranium was found. [27] It was found that at dosages above 6 L, (L = langmuir), CO is physisorbed on all samples and at temperatures at and above 300°K only dissociative CO adsorption is possible. Oxidation of uranium involves the adsorption of reactant gas molecules onto the metal surface, their dissociation into atomic species, and the chemical binding of the gas atoms with surface uranium atoms. It was found that as this process continues, an oxide layer begins to form which eventually covers the entire surface. [28] Subsequent oxidation requires the diffusion of adsorbed gas atoms through the oxide layer and this diffusion process is profoundly influenced by the defect structure and electronic properties of the oxide layer. It was shown that no potential energy barrier is needed for the uranium and O_2 to form the metastable states, while a very little barrier is needed to form stable linear UO₂ from the metastable structures and that the uranium 5f atomic orbital electrons dominate in the formation of the U - O bonds. [29] For investigating the details of the crystal structure, axial ratios of α -uranium as a function of pressure were measured and compared with first-principles theory. [30] Of the two axial ratios, the c/a ratio was more sensitive to pressure and the theory accurately reproduced the experimental finding of a pressure induced increase of the c/a axial ratio. Uranium, being the heaviest naturally occurring element, has received a lot of attention for its nuclear properties and the nuclear energy that can be harvested. Less discussed are the properties of uranium metal which are largely determined by its electrons surrounding the nuclei in the solid. Interesting properties of uranium include low temperature charge density waves transitions, [31] anisotropic thermal expansion, [32] and a relatively complex crystal structure (orthorhombic).[33]

On the theoretical side, using the linear combination of Gaussian type orbitals – fitting function (LCGTO-FF) method within the GGA approximation of density functional theory (GGA-DFT), Boettger and Ray have carried out detailed electronic structure studies of crystalline UO_2 and its magnetic ordering [34-35]. Hybrid density functional theory with relativistic effective core potentials (RECP) has been used by Kudin et al. [36] to study the insulating gap of UO₂. The density functional study of O_2 adsorption on (100) surface of γ -uranium shows that dissociative adsorption of O₂ is more favorable compared to molecular adsorption [16]. Recently, the gas-phase chemi-ionization reaction between uranium and oxygen atoms have been studied theoretically and potential energy curves have been calculated [37]. A thermodynamic assessment of the uranium-oxygen system has been presented by Gueneau et al [38]. A consistent set of experimental data was selected among numerous data on the phase diagram and oxygen chemical potential. It concluded that a three sub-lattice model is suitable to describe complex oxides such as $UO_{2\pm x}$. The main goal of our work is to present a detailed electronic and geometric structure study of the initial stages of atomic oxygen and carbon chemisorption on the (100) surface of γ -uranium by using *ab initio* methods. It was found that density functional theory, in its GGA (Generalized Gradient Approximation) formulation, accurately describes the electronic structure of uranium, and possible correlation effects are well accounted for within this theory.[39] Also the structure of uranium was investigated by a plane-wave pseudopotential technique. [40] Using relativistic density functional theory to parameterize the uranium element by using the dimer interaction potential energy profile of U₂, it was found that uranium microclusters prefer to form three-dimensional compact structures. [41]

CHAPTER 2

THEORY

2.1 Density Functional Theory

2.1.1 Introduction

Most electronic structure calculations for solids are based on density functional theory (DFT), which results from the work of Hohenberg, Kohn and Sham. [42, 43] Moreover density functional theory is currently the most popular method in condensed matter physics and quantum chemistry for solving the many body quantum mechanical problems. In this chapter we describe the density functional method for electronic structure calculations. We first present the physical interpretation of the density functional equations followed by there formal derivations. Conceptually simpler and formally rigorous density functional theory provides an elegant way of mapping a Nvariable system to a single variable, the system's density, and hence reducing the computational cost significantly over the traditional ab initio theories such as Hartree-Fock theory, while retaining the much of the computational accuracy. In principal, density functional theory is an 'exact' theory and is applicable to any interacting system with an external potential. Approximations enter while treating the exchange-correlation effect by the functionals and the accuracy of the calculations depends on the representibility of the functionals, though the conditions for the representability of the functionals are still not well defined. However, continual developments of the

functionals by including the local, semi-local and, recently, the dynamic effects (in DFT nomenclature these are called LDA, GGA and meta-GGA, respectively) increase the predictability and accuracy of computations. In the following we will present a short description of density functional theory following mostly the reviews of Yang and Parr [44-46], Capelle [47] and Nagy [48-50].

2.1.2 Hohenberg-Kohn Theorem

Let us consider a system of *N* electrons under the influence of some timeindependent external potential. Hohenberg-Kohn theorem states that, the external potential $v(\vec{r})$ is determined solely by the electron density $\rho(\vec{r})$, within a trivial additive constant. The basic difference from the traditional quantum mechanics is that in density functional theory we solve for the density rather than the wave functions. Of course densities are defined from the wave function in a very trivial manner:

$$\rho(\vec{r}_1) = N \int \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) ds_1 d\vec{x}_2 d\vec{x}_3 \dots d\vec{x}_N$$
(2.1)

where Ψ is assumed to be normalized to unity; and \bar{x}_i 's include both spin and spatial variables which, in equation (1) are integrated out for i = 2 to N, including the spin part of the first particle. So once the density of electrons is known the other electronic properties can also be computed. For example, the total number of electrons is given by:

$$N = \int \rho(\vec{r}) d\vec{r} \tag{2.2}$$

Also from Kato's theorem [51], which is applicable only to the Coulomb potential, we get:

$$Z_{\beta} = -\frac{1}{2\rho(\vec{r})} \frac{\partial\rho(\vec{r})}{\partial r} \bigg|_{r=R_{\beta}}$$
(2.3)

where the partial derivatives are taken at the nuclei β . So from the equation (3) we see that from the cusps of the density define the position of the nuclei, R_{β} , and the atomic number Z_{β} . In general $v(\vec{r})$ in the Hohenberg-Kohn theorem is not restricted to the Coulomb potentials.

Let us now proceed to prove the Hohenberg-Kohn theorem following the original approach of their papers. The original proof was both simple and elegant, and was done by reduction ad absurdum, basically for the non-degenerate systems. However the general conclusion is applicable to degenerate system as well. The proof follows like this:

Let us suppose that, in addition to $v(\vec{r})$ there exists another potential $v'(\vec{r})$ due to the same density $\rho(\vec{r})$, and that $v(\vec{r}) \neq v'(\vec{r}) + c$, where c is just an additive constant. Now due to this two potentials we will have two ground state wave functions Ψ and Ψ' corresponding to two Hamiltonian H and H' with the ground state energies of E and E', respectively. The Hamiltonians are defined as:

$$H = T + V_{ee} + \sum_{i}^{N} v(\vec{r}_{i}), \qquad (2.4)$$

where T and V_{ee} are the kinetic energy and electron-electron repulsion operators defined as below:

$$T = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} , \qquad (2.5)$$

$$V_{ee} = \sum_{i (2.6)$$

Here we use the atomic units where

$$e^2 = \hbar = m_e = 1.$$

where *e* is the electronic charge, \hbar is the Plank's constant and m_e is the electron mass. In this unit energies are given in Hertrees, 1H = 27.2116 eV = 627.4 kcal/mol and the distances are in Bohr, $a_o = 0.529 \text{ Å}$.

From Rayleigh_Ritz variational principal it follows that

$$E_{0} = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H | \Psi' \rangle + \langle \Psi' | H - H' | \Psi' \rangle$$
$$= E_{0}' + \int \rho(\vec{r}) [v(\vec{r}) - v'(\vec{r})] dr \qquad (2.7)$$

Similarly, using the variational principle for the Hamiltonian H' with the trial wave function Ψ , we have

$$E'_{0} = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H | \Psi \rangle + \langle \Psi | H' - H | \Psi \rangle$$
$$= E'_{0} + \int \rho(\vec{r}) [v(\vec{r}) - v'(\vec{r})] dr \qquad (2.8)$$

Addition of equation (2.7) and (2.8) leads to

$$E_0 + E_0' < E_0' + E_0 \tag{2.9}$$

which clearly is a contradiction, so we can conclude that given the electronic density, the external potential is determined, so as all the other electronic properties, for example total energy.

Let us write the total energy as,

$$E_{v}(\rho) = T(\rho) + V_{ne}(\rho) + V_{ee}(\rho)$$
$$= \int \rho(\vec{r}) \Psi(\vec{r}) d\vec{r} + F_{HK}[\rho]$$

where,

$$F_{HK}[\rho] = T(\rho) + V_{ee}[\rho]$$
(2.11)

Here, V_{ee} includes both the classical and non-classical (for example, Coulomb and exchange interactions) contributions and F_{HK} is the Hohenberg-Kohn functional, which does not depend on the external potential as can be seen from equation (2.11) and so is a universal functional of $\rho(\vec{r})$.

The second Hohenberg-Kohn theorem states that for a trial density $\tilde{\rho}(\vec{r})$, such that $\tilde{\rho}(\vec{r}) \ge 0$, and $\int \tilde{\rho}(\vec{r}) d\vec{r} = N$,

$$E_0 \le E_v \left[\tilde{\rho} \right] \tag{2.12}$$

where, $E_{\nu}[\tilde{\rho}]$ is the energy functional of equation (2.10). The proof will be done by the use of variational principle. For any trial density $\tilde{\rho}(\bar{r})$, according to the Hohenberg-Kohn first theorem, it has its won potential $\nu(\bar{r})$, Hamiltonian *H* and wave function $\tilde{\Psi}$. So we get following equation (2.10),

$$\left\langle \widetilde{\Psi} \left| H \right| \widetilde{\Psi} \right\rangle = \int \widetilde{\rho}(\vec{r}) v(\vec{r}) d\vec{r} + F_{HK} = E_{v}[\widetilde{\rho}] \ge E_{v}[\rho]$$
(2.11)

Now the variation of total energy with the constraint that the total electrons are fixed, we get,

$$\delta\left\{E_{\nu}[\rho] - \mu\left[\int \rho(\bar{r})d\bar{r} - N\right]\right\} = 0$$
(2.12)

which leads to the Euler-Lagrange equation

$$\mu = \frac{\delta E_{\nu}[\rho]}{\delta \rho(\bar{r})} = \nu(\bar{r}) + \frac{\delta F_{HK}}{\delta \rho(\bar{r})}$$
(2.13)

where the Lagrange multiplier μ is the chemical potential. Now if the exact form of the functional F_{HK} is known, the equation (2.12) then would be an exact equation for the ground state electron density. The functional F_{HK} is defined only for those trials $\rho(\vec{r})$ which are *v*-representable, meaning that the $\rho(\vec{r})$ corresponds to a anti-symmetric ground state wave function of some Hamiltonian with external potentials $v(\vec{r})$. The conditions for the density to be *v*-representable is yet unknown. However it turned out that the density functional theory can be formulated on a density which satisfies a weaker constraint than that of *v*-representability, namely *N*-representability. A density is *N*-representable if it can be derived from some anti-symmetric wave functions. Based on the *N*-representable density, Levy's constrained search method is described below which eliminates the degeneracy limitations in the proof of original Hohenberg-Kohn theorem.

2.1.2.1 The Method of Constrained Search

This method was first developed by Levy and Lieb [52-55]. A Universal function $F[\rho]$ defined as a sum of kinetic and Coulomb repulsion energies:

$$F[\rho] = \underset{\Psi \to \rho}{\text{Min}} \langle \Psi | T + V_{ee} | \Psi \rangle$$
(2.14)

 $F[\rho]$ searches all wave functions Ψ which yield the fixed trial density ρ , and ρ need not to be *v*-representable.

Now the ground state energy can be written as:

$$E_{0} = \underset{\Psi \to \rho}{Min} \langle \Psi | T + V_{ee} + \sum_{i}^{N} v(r_{i}) | \Psi \rangle$$

$$= \underset{\rho}{Min} \left\{ \underset{\Psi \to \rho}{Min} \langle \Psi | T + V_{ee} + \sum_{i}^{N} v(r_{i}) | \Psi \rangle \right\}$$

$$= \underset{\rho}{Min} \left\{ \left[\underset{\Psi \to \rho}{Min} \langle \Psi | T + V_{ee} | \Psi \rangle + \int v(\bar{r}) \rho(\bar{r}) d\bar{r} \right] \right\}$$

$$(2.15)$$

Now using the definition of $F[\rho]$ from equation (2.14) we can write equation (2.16) as:

$$E_{0} = \underset{\rho}{Min} \left\{ F[\rho] + \int v(\vec{r})\rho(\vec{r})d\vec{r} \right\}$$
$$= \underset{\rho}{Min} E[\rho]$$
(2.17)

where

$$E[\rho] = F[\rho] + \int v(\vec{r})\rho(\vec{r})d\vec{r}.$$
(2.18)

In the constrained search formula for the functional $F[\rho]$ there is no reference that ρ needs to be *v*-representable ground state density, as long as it is constructed from an anti-symmetric wave function. However, when ρ is *v*-representable we get:

$$F[\rho] = F_{HK}[\rho] \tag{2.19}$$

The functional $F[\rho]$ is universal because it does not depend on the external potential $v(\bar{r})$. This constrained search method remove the degeneracy problem from the original Hohenberg-Kohn theorem, for in the approach only one of a set of degenerate wave functions is selected which is corresponding to the given ρ .

2.1.3 The Kohn-Sham Method

The ground state electron density can be in principle determined by solving the Eular-Lagrange equation

$$\frac{\delta F(\rho)}{\delta \rho} + v(\bar{r}) = \mu.$$
(2.20)

where μ is the Lagrange multiplier associated with the constraint:

$$\int \rho(\vec{r}) d\vec{r} = N$$

Here the exact form of the functional $F[\rho]$ in equation (2.20) is not known:

$$F(\rho) = T[\rho] + V_{ee}[\rho]. \qquad (2.21)$$

As can be seen from the above equation the basic problem is to evaluate the kinetic energy term. Kohn-Sham proposed an indirect approach to this problem, which is described in the following.

Let us consider a non-interacting system where electrons move independently in a common local potential v_s , where the electronic density $\rho(\vec{r})$ is the same as the interacting electronic system. This can be done as long as we ensure that the wave functions, from which $\rho(\vec{r})$ is constructed, are *N*-representable. Hamiltonian is:

$$H_s = \sum_i^N \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_i^N v_s(\vec{r}_i).$$
(2.22)

In the above Hamiltonian there is non electron-electron repulsion term. For this system we can write the non-interacting wave-function as the Slater determinant:

$$\Psi_s = \frac{1}{\sqrt{N!}} \det[\psi_1 \psi_2 \cdots \psi_N]$$
(2.23)

where ψ_i are the N lowest eigenstates of the one-electron Hamiltonian h_s :

$$h_{s}\psi_{i} = \left[-\frac{1}{2}\nabla_{i}^{2} + v_{s}\left(\bar{r}_{i}\right)\right]\psi_{i} = \varepsilon_{i}\psi_{i} \qquad (2.24)$$

The kinetic energy of this non-interacting system is,

$$T_{s}[\rho] = \left\langle \Psi_{s} \left| \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_{i}^{2} \right) \right| \Psi_{s} \right\rangle = \sum_{i}^{N} \left\langle \psi_{i} \left| -\frac{1}{2} \nabla_{i}^{2} \right| \psi_{i} \right\rangle$$
(2.25)

while the density of the non-interacting system

$$\rho(\vec{r}) = \sum_{i}^{N} |\psi_i(\vec{x}_i)|^2 \qquad (2.26)$$

is equal to that of the interacting one.

The kinetic energy functional $T[\rho]$ in equation (2.21), as mentioned before, is unknown, so we simply take the kinetic energy functional $T_s[\rho]$ of non-interacting system instead of $T[\rho]$. Let the difference between this two functional is $T_c = T - T_s$, and substituting this in equation (21) we get:

$$F[\rho] = T_s[\rho] + V_{ee}[\rho] + T_c[\rho]$$
(2.27)

The last two terms in the right hand side of equation (2.27) representing the electronelectron interaction and we can rewrite them as the Coulomb and exchange-correlation terms, respectively:

$$V_{ee}[\rho] + T_c[\rho] = J[\rho] + E_{xc}[\rho]$$
(2.28)

So equation (2.27) can be written as:

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$
(2.29)

So with the above functional the total energy of equation (2.18) can be written as:

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int \rho(\vec{r}) v(\vec{r}) d\vec{r} . \qquad (2.30)$$

Now the variation of equation (2.30) gives the Euler-Lagrange equation:

$$\mu = \frac{\delta E[\rho]}{\delta \rho} = \frac{\delta}{\delta \rho} \int \rho(\vec{r}) v(\vec{r}) d\vec{r} + \frac{\delta T_s[\rho]}{\delta \rho} + \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho}$$
$$= v(\vec{r}) + \frac{\delta T_s[\rho]}{\delta \rho} + \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho}$$
(2.31)

$$= v_{eff}(\vec{r}) + \frac{\delta I_s[\rho]}{\delta \rho}$$
(2.32)

where the Kohn-Sham effective potential is defined by:

$$v_{eff} = v(\vec{r}) + \frac{\delta I[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho}$$
$$= v(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{xc}(\vec{r})$$
(2.33)

here we also defined the exchange-correlation potential as:

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}(\rho)}{\delta \rho}$$
(2.34)

Now let us rewrite equation (2.30) in terms of one electron orbitals:

$$E(\rho) = \sum_{i}^{N} \int \psi_{i}^{*} \left(-\frac{1}{2} \nabla^{2} \right) \psi_{i} d\vec{r} + J(\rho) + E_{xc}[\rho] + \int v(\vec{r}) \rho(\vec{r}) d\vec{r}$$
(2.35)

and the electron density is, as in equation (2.26):

$$\rho(\vec{r}) = \sum_{i}^{N} \left| \psi_{i} \right|^{2}$$

So in equation (2.35) energy is expressed in terms of N orbitals.

Now taking the variation of energy in equation (2.35) with respect to the one-electron orbital ψ_i , along with the constraint that these oribitals are orthonormal to each other:

$$\int \psi_i^* \psi_j d\bar{x} = \delta_{ij} \tag{2.36}$$

We get,

$$\delta \left[E[\rho] - \sum_{i}^{N} \sum_{j}^{N} \varepsilon_{ij} \int \psi_{i}^{*}(\bar{x}) \psi_{i}(\bar{x}) d\bar{x} \right] = 0$$
(2.37)

In equation (2.37) ε_{ij} are the Lagrange multipliers. Let us now consider the variation in the energy $E[\rho]$ given by the equation (2.35),

$$\delta E[\rho] = \left[\frac{\delta}{\delta \psi_i^*} \sum_{i}^{N} \int \psi_i^* \left(-\frac{1}{2} \nabla^2\right) \psi_i d\vec{r} + \frac{\delta I}{\delta \psi_i^*} + \frac{\delta E_{xc}}{\delta \psi_i^*} + \frac{\delta}{\delta \psi_i^*} \int v(\vec{r}) \left(\sum_{i}^{N} |\psi_i|^2\right) d\vec{r} \right] \delta \psi_i^*$$
(2.38)

Using chain rule for functional derivative, the first term in the right hand side gives,

$$\frac{\delta}{\delta\psi_{i}^{*}}\sum_{i}^{N}\int\psi_{i}^{*}\left(-\frac{1}{2}\nabla^{2}\right)\psi_{i}d\vec{r} = \frac{\partial\psi_{i}^{*}}{\partial\psi_{i}^{*}}\left(-\frac{1}{2}\nabla^{2}\right)\psi_{i} + \psi_{i}^{*}\frac{\partial}{\partial\psi_{i}^{*}}\left\{\left(-\frac{1}{2}\nabla^{2}\right)\psi_{i}\right\}$$
$$= -\frac{1}{2}\nabla^{2}\psi_{i} \qquad (2.39)$$

where derivative in the second term is zero. Similarly the last term in the variation of energy in equation (2.38) gives,

$$\frac{\delta}{\delta \psi_i^*} \int v(\vec{r}) \left(\sum_{i}^{N} |\psi_i|^2 \right) d\vec{r} = v(\vec{r}) \psi_i$$
(2.40)

So from equation (2.37), for any arbitrary variation of $\delta \psi_i^*$, we get using equations (2.39) and (2.40),

$$h_{eff} \psi_{i} = \left[-\frac{1}{2} \nabla^{2} + \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho} + v(\vec{r}) \right] \psi_{i} = \sum_{j}^{N} \varepsilon_{ij} \psi_{j}$$
$$\Rightarrow h_{eff} \psi_{i} = \left[-\frac{1}{2} \nabla^{2} + v_{eff}(\vec{r}) \right] \psi_{i} = \sum_{j}^{N} \varepsilon_{ij} \psi_{j} \qquad (2.41)$$

where $v_{eff}(\vec{r})$ is defined by equation (2.33). Now in equation (2.41) the Hamiltonian h_{eff} is a Hermitian operator, hence ε_{ij} is a Hermitian matrix which can be diagonalize by unitary transformation, which leads to the Kohn-Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\vec{r})\right]\psi_i = \varepsilon_i\psi_i$$
(2.42)

Equation (2.42) (or equation (2.41)) is the central equation in the application of density function theory. These equations are usually solved by self-consistent methods which can be represented by the following flow-chart:



Figure 2.1 Flow-chart for DFT self-consistency loop

The solution of Kohn-sham equation is in principle is exact, but as can be seen from the above discussion of the Kohn-Sham procedure that, it does not give any prescription of obtaining the exchange-correlation functionals. Depending on the system at hand, different levels of approximations were made to deal with this functional. In the following we will describe the local and generalized density approximations to these functionals.

2.1.4 Generalized Gradient Approximation: GGA

Logically the first step to improve upon the LDA is to take into account the spatial change in electronic density, i.e., the gradient of the density, $\nabla \rho(\vec{r})$, to take into account the non-homogeneity of the true electron density. This method is named as the gradient expansion approximation (GEA). This can be done by a Taylor series expansion of the exchange-correlation functional,

$$E_{xc}^{GEA}[\rho_{\alpha},\rho_{\beta}] = \int \rho(\vec{r})\varepsilon_{xc}(\rho_{\alpha},\rho_{\beta})d\vec{r} + \sum_{\sigma,\sigma'}\int C_{xc}^{\sigma,\sigma'}(\rho_{\alpha},\rho_{\beta})\frac{\nabla\rho_{\sigma}}{\rho_{\sigma'}^{2/3}}\frac{\nabla\rho_{\beta}}{\rho_{\sigma'}^{2/3}}d\vec{r} + \cdots \quad (2.53)$$

The coefficient $C_{xc}^{\sigma,\sigma'}$ in equation (53) was found to be proportional to $1/\rho^{4/3}$. Unfortunately, GEA did not give a systematic improvement on the LDA approximation. The reason is that the exchange correlation interaction was not found physically very meaningful in this definition. In addition to it, higher order corrections of $\nabla \rho$'s are exceedingly difficult to calculate. However, a more sophisticated approach to include the gradient of densities was proposed by Perdew and others [56-59]generalized
gradient approximation (GGA), which defines the exchange-correlation functional in the following manner,

$$E_{xc}^{GGA}[\rho_{\alpha},\rho_{\beta}] = \int f(\rho_{\alpha},\rho_{\beta},\nabla\rho_{\alpha},\nabla\rho_{\beta}) d\vec{r}$$
(2.54)

In practice, E_{xc}^{GGA} is divided into its exchange and correlation contributions,

$$E_{xc}^{GGA} = E_x^{GGA} + E_c^{GGA}, \qquad (2.55)$$

and the approximations for the functionals are usually made individually.

Several suggestions for the explicit dependence of f on the densities and their gradient have been proposed over the year, including the functionals which include the parameters which are calibrated against some reference systems. Among the most widely used functionals are the 1986 Perdew functions, where the correlation functional contained on empirical parameter. The Perdew-Wang 1991 functional (PW91) incorporates no empirical parameters and is determined from the uniform electron gas approximations and with exact constraints. A refinement on PW91 was done by Perdew, Burke and Ernzerhof, the PBE functional [60-61]. Another popular functional for correlation is due to Lee, Yang and Parr (LYP) [59], which is not based on uniform electron gas, and obtained the correlation energy as an explicit functional of the density, its gradient. The LYP functional contained one empirical parameter. This correlation functional is often combined with Becke's exchange functional [62-63] and is known as BLYP.

It should be mentioned in here that GGA does not provide a complete non-local functional. In true mathematical sense, $\rho(\vec{r})$, and its gradient $\nabla \rho(\vec{r})$ depends only on

 \vec{r} , and is independent of any $\rho(\vec{r}')$, where $\vec{r}' \neq \vec{r}$. Only advantage GGA achieved is that it includes the local variation of the densities. Also GGA in its original form does not produce the simultaneous asymptotic behavior for both the energy and the potentials. In the modern day functionals, a cut-off procedure on density is used to produce the satisfactory results. However, GGA functionals does show improvements over LDA functionals in many systems in condensed matter physics and quantum chemistry, with the exception in the long range weakly bound system, for instance in van der Waals interaction.

2.2 Scalar Relativistic Approximations

For the heavier atoms in the periodic table relativistic corrections to the electronic energy levels are important. A frequently cited example is that without relativistic corrections to the energy level calculation of gold atoms, its color would look like silver. Also if we consider one electron motion around an Hg nucleus, the relativistic mass corrections for the electron is almost 23% and the speed of the electron is almost 53% of the speed of light. In the following we present a short introduction of scalar relativistic approximations.[70]

The four-component Dirac equation can be written as,

$$i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t} = \left(c\alpha \cdot \hat{p} + \beta mc^2\right) \Psi(\vec{r},t)$$
(2.56)

where $\Psi(\vec{r},t)$ is a four-component wave-function:

$$\Psi(\vec{r},t) = \Psi(\vec{r})e^{-iWt} = \begin{pmatrix} \Psi_1(\vec{r}) \\ \Psi_2(\vec{r}) \\ \Psi_3(\vec{r}) \\ \Psi_4(\vec{r}) \end{pmatrix} e^{-iWt}$$
(2.57)

and, $W = \alpha \cdot pc + \beta mc^2$.

Here α and β are 4 × 4 matrices, which has the following properties,

$$\alpha^2 = \beta^2 = 1, \ \{\alpha, \beta\} = 0 \text{ and } \{\alpha_i, \alpha_j\} = 0.$$

Here the $\{\ \}$ represents the anti-commutation.

It is very difficult to solve 4-component Dirac equations for a large system. One approach is to use Breit-Pauli Hamiltonian, which is a limit of the Dirac equation in Hermitian form, correct to the order of $\frac{1}{c^2}$:

$$H_{BP} = H_0 + H_{MV} + H_D + H_{SO}$$
(2.58)

where, H_0 is the non-relativistic Hamiltonian, H_{MV} is the mass-velocity term,

$$H_{MV} = -\frac{\alpha^2}{8} \sum_i p_i^4 \, .$$

 H_D is the Darwin term, $H_D = \frac{\alpha^2}{8} (\nabla^2 V)$, and the potential V is given by,

 $V = -Z\sum_{i} \frac{1}{r_i} + \sum_{i < j} \frac{1}{r_{ij}}$. This is a contribution to the energy that has no classical analogue.

It comes from the fact that electron cannot be regarded as a point particle but is spread out over a volume of the order of Compton wave-length: $(\hbar^3/mc)^3$.

 H_{so} is the spin-orbit coupling term,

$$H_{SO} = \frac{\alpha^2}{2} \left(\sum_i \frac{Z}{r_i^3} (L_i \cdot S_i) - \sum_{i \neq j} \frac{1}{r_{ij}^3} (r_{ij} \times P_i) \cdot (S_i + 2S_j) \right).$$

In all of the above equations, α is the fine structure constant. In the scalar relativistic approximations this term is not included in the calculations.

CHAPTER 3

ADSORPTION OF OXYGEN AND CARBON ON (100) SURFACE OF γ -URANIUM

In this chapter, first we give a brief outline about the computational details and the theory used for our calculations, followed by the discussion of our results on the atomic adsorption of oxygen and carbon on U (100) surface. As in some of our previous works [16, 64-72], all computations reported here have been performed at the spin restricted and unrestricted generalized gradient approximation (GGA) level to density functional theory (DFT) [73-79], using the DMol3 suite of programs [80]. In DMol3, the physical wave function is expanded in 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 and a real space cut-off of 5.0 Å were used. The sizes of these DNP basis sets are comparable to the 6-31G** basis set of Hehre et al [81]. However, they are believed to be 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, called density functional semi-core pseudopotential (DSSP) was used [80]. These norm-conserving pseudo-potentials were generated by fitting allelectron relativistic DFT results and have a non-local contribution for each channel up to l = 2, as well as a nonlocal 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 [82]. 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 ultra-thin film (UTF) of uranium could be magnetic due to local magnetic ordering at the narrower electronic bands on the surface. From nuclear magnetic resonance data in UO₂, it was predicted that UO₂ becomes a non-collinear anti-ferromagnet below 30.8 °K [83]. 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 are concerned, 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 [80] 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. Boettger and Ray [25-26] noted in their uranium dioxide study that the spin-polarized induced splitting of U 5f bands is roughly 1.0eV, compared to the spin-orbit splitting of 0.3eV. Hay and

Martin [84] found that one could adequately describe the electronic and geometric properties of actinide complexes without treating spin-orbit effects explicitly. Similar conclusions have been reached by Ismail *et al.* [85] in their study of uranyl and plutonyl ions. We also note, as mentioned before, that scalar-relativistic hybrid density functional theory has been used by Kudin *et al.* [27] to describe the insulating gap of UO_2 , yielding a correct anti-ferromagnetic insulator. All calculations are done on a Compaq ES40 alpha multi-processor supercomputer at the University of Texas at Arlington.

To study atomic oxygen and carbon adsorption on the γ -uranium (100) surface, we modeled the surface with three layers of uranium at the experimental lattice constant. This is believed to be adequate considering the oxygen and carbon atoms are not expected to interact with uranium 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 [64-72]. Also, recently, using the linear combinations of Gaussiantype orbitals fitting function (LCGTO-FF) method, Ray and Boettger showed in a study of quantum size effects of non-spin-polarized δ -plutonium (111) and (001) surfaces that surface energies converge within the first three layers [86]. The same was found to be true by Wu *et al.* for δ – Pu (001), (110), and (111) surfaces, using the spin-polarized full-potential linearized-augmented-plane-wave (FP-LAPW) method [87]. Due to severe demands on computational resources, the unit cell per layer was chosen to contain four uranium atoms and no surface relaxations and/or reconstructions were taken into account. Thus, in *some* sense, the results reported here can be considered as preliminary. However, relaxations and/or reconstructions of actinide surfaces, if any, are expected to be small and the qualitative and quantitative conclusions reached in this study are expected to be valid in any future investigations taking into account full relaxations and reconstructions. Thus, our three layer model of the surface contains 12 uranium atoms. The oxygen atom and carbon atom, one per unit cell, were allowed to approach the uranium surface along four different symmetrical approaches: i) directly on top of a U atom (*top* position) (Fig.1); ii) on the middle of two nearest neighbor U atoms (*bridge* position) (Fig.2); iii) in the center of the smallest unit structures of the surfaces (*center* position) (Fig.3); iv) inside the U layers (*interstitial* position) (Fig.4). The chemisorption energy is calculated from:

$$E_c = E (U-layers) + E (X) - E (U-layers + X);$$
 $X = O, C$

For the non-spin polarized case, both E (U-layers) and E (U-layers + X) were calculated without spin polarization, while for spin polarized calculations, both of these two energies are spin polarized. E (X) is the energy of the oxygen and carbon atoms in the ground state.

We first comment on the oxygen adsorption on the γ -U (100) surface. The chemisorption energies as a function of the separation distance of the O atom from the top layer for four different approaches, including non-spin-polarized (NSP) and spin-polarized (SP) cases, are shown in Figs. 5 – 12. In Tables 3.1 and 3.2, we have listed the chemisorption energies and the equilibrium distances of the O atom from the top layer for the NSP and SP levels of theory. Also, the magnetic moments in μ_B per atom for the spin polarized case are given in the last column of Table 3.2. At the non-spin-polarized

level of theory, the bridge site is the most favorable chemisorbed site with chemisorption energy of 7.887eV, followed by the center, top and the interstitial sites, with chemisorption energies of 7.658eV, 7.237eV, and 0.879eV respectively. For the bridge position, the distance of the oxygen atom from the top layer has the lowest value of 1.19 Å, with the nearest O - U distance being 2.133 Å. For the center position, the distance of the oxygen atom from the surface is 0.66 Å, with four U atoms at the corners of the square being 3.467 Å apart and the nearest O - U distance being 2.533 Å. For the top position, where oxygen atom is directly on top of one of the uranium atom, the distance is 1.86 Å. For the interstitial position, the oxygen atom lies inside the three layer slab. Here the chemisorption energies for the bridge and the center sites are very close and differ by 0.229eV. In view of the above picture of distance versus chemisorption energy, we conclude that the two sites, bridge and center, with the coordination number of two and four respectively, are more favorable compared to the top site with a coordination number of one. The interstitial site is the least favorable as its interaction with the top layer is considerably low.

A similar picture can be drawn for the spin polarized calculations. With the inclusion of spin polarization, the chemisorption energies are consistently higher than the non-spin-polarized cases though the differences in energies between the non-spin-polarized and spin-polarized cases are not very significant. On the other hand, a consistent trend can not be observed for the adsorption distances. We note however that the bridge site is again the most favorable site for oxygen adsorption. For the spin polarized case, the chemisorption energies for bridge, center, top, and interstitial sites

are 7.965eV, 7.797eV, 7.261eV, and 0.926eV and the adsorption distances are 1.22 Å, 0.64 Å, 1.86 Å, and 1.71 Å respectively. For the most favorable adsorption site, the bridge position, the chemisorption energy is higher by 0.078eV for the spin polarized case, compared to the non-spin-polarized case. To study the effects of spin polarization, we also calculated the spin magnetic moments for different chemisorption sites of the oxygen adatom, which are listed in Table 3.2. The magnetic moments of the bare uranium layers drop rapidly as the number of layers increase, from $4.345\mu_{\rm B}$ per atom for the monolayer to $1.610\mu_B$ per atom for the 3-layer. This indicates that the semi-infinite uranium metal surface might indeed be paramagnetic. Moreover, our value for the magnetic moment of three layers of uranium slab is higher than the spin magnetic moment of $0.84\mu_{\rm B}$ per atom for α -uranium predicted using the full-potential-linearizedaugmented-plane-wave method in the generalized gradient approximation [88]. The adsorption of oxygen adatom on the U (100) surface reduces the magnetic moments of the system. The bridge site has the highest magnetic moment of $0.167\mu_{\rm B}$ per atom, which is also the most favorable site for oxygen adsorption. The top, center, and interstitial sites have a magnetic moment of $0.158\mu_B$, $0.021\mu_B$, and $0.008\mu_B$ per atom, respectively. Table 3.3 lists the spin and Mulliken charge distribution [89-91] for the most stable chemisorption site in the spin polarized case, namely, the bridge site. The charge distribution for the bare uranium layers show that in the first and the third layer all the atoms have negative charges, 0.079e each, while in the second layer all the atoms have positive charges, 0.158e each. After oxygen adsorption, as expected, the oxygen atom acquires negative charge, 0.618e, primarily from the first layer of uranium. In the

first layer the charge distribution is changed due to oxygen adsorption and two of the atoms are now positively charged. The charge distributions for second and the third layers do not change significantly indicating, as expected, the oxygen adatom interacts primarily with the atoms in the first layer. For the bare uranium layers, analysis of the spin distribution shows that spins of all the atoms are aligned in the same direction. After oxygen adsorption, the spins of uranium atoms in all the three layers changes, which is noteworthy. Thus it can be concluded that even though the charge distributions of the uranium slab after oxygen adsorption for the second and third layer do not change significantly, the spin distribution of the uranium slab, as a whole changes notably after oxygen adsorption. This can be also seen from the drop of magnetic moment, from $1.610\mu_B$ per atom for the bare uranium layers to $0.167\mu_B$ per atom for the oxygen adsorbed bridge site. Also charge and spin distribution tables for other chemisorption sites, top, center and interstitial are given in Table 3.6, Table 3.7 and Table 3.8 respectively.

Comparing our results of oxygen adsorption on U (100) surface with our previous work on oxygen adsorption on Pu (100) surface [64-72] (from Tables 3.1 and 3.2), it can be seen that the most favorable site for adsorption on Pu (100) surface is the center site with chemisorption energies of 7.386eV for the non-spin polarized and 7.080eV for the spin polarized cases, whereas the most favorable site for adsorption on U (100) surface is the bridge site with 7.887eV and 7.965eV for the non-spin and spin polarized cases respectively. Thus, we can infer that the oxygen adatom interaction is stronger with the uranium surface than with the plutonium surface. The differences

between the two surfaces become more pronounced when we include spin polarization in the calculations. Oxygen chemisorption energies on a spin-polarized U (100) surface are consistently higher compared to a non-spin-polarized surface but for the Pu (100) surface, the chemisorption energies for the spin-polarized Pu (100) surface are consistently lower. Though interstitial site is found to be the least favorable for both the cases, the chemisorption energies for the interstitial site of Pu (100) surface (5.422eV and 5.334eV for non-spin and spin polarized cases) are considerably higher than that for the U (100) surface (0.879eV and 0.926eV for non-spin and spin polarized cases). This is partly attributed to the fcc structure of δ – Pu, compared to the bcc structure of γ – U. For the interstitial site of Pu (100) surface, the oxygen atom is surrounded by six Pu atoms at equal distances of 2.14Å. For the interstitial site of U (100) surface, the oxygen atom is surrounded by four U atoms at equal distances of 2.458Å. Due to this geometrical difference, the oxygen atom interacts more strongly with the Pu atoms in the interstitial site inside the plutonium slab compared to the interstitial site of the uranium slab and hence exhibits a higher probability of being chemisorbed. For both cases, however, as noted before, the oxygen adatom interacts mainly with the first layer atoms of the uranium or plutonium surface, with the second and the third layer being affected only slightly. Also the magnetic moments for different chemisorption sites are found to be significantly higher in case of Pu (100) surface, compared to U (100) surface, indicating a stronger magnetic nature of the Pu surface.

For carbon adsorption on γ -uranium (100) surface, the chemisorption energies and the corresponding equilibrium distances of the carbon adatom from the uranium top layer are given in Table 3.3. Also, the magnetic moments in $\mu_{\rm B}$ per atom for the spin polarized case are given in the last column. The chemisorption energies as a function of the separation distance of the C atom from the top layer for four different approaches are shown in Figs. 13-20. For non-spin-polarized calculations, the center site is the most favorable chemisorbed site with chemisorption energy of 7.816eV, followed by the bridge, top, and the interstitial sites, with chemisorption energies of 6.551eV, 4.486eV, and 1.974eV, respectively. This is contrary to the case of oxygen adsorption, where, for the non-spin-polarized case, bridge site was the most favorable site for chemisorption. For the center position, the distance of carbon atom from the top layer has the lowest value of 0.62 Å, with four uranium atoms at the corners of the square being 3.467 Å apart and the nearest C - U distance being 2.538 Å. For the bridge position, the distance of the carbon atom from the top layer has the next higher value of 1.13 Å, with the nearest C – U distance being 2.065 Å. For the top position, where the carbon atom is directly on top of one of the uranium atom, the distance is 1.88 Å. For the interstitial position, the carbon atom lies inside the three layer slab with a chemisorption energy of 1.974eV for the non-spin polarized case (1.981eV for spin polarized case). For oxygen, the chemisorption energies for the interstitial site are 0.879eV and 0.926eV for non-spin and spin polarized cases, respectively. This is in agreement with the experimental results of McLean et al [21]. Their results indicate that, upon adsorption of carbon and oxygen on the uranium surface, the oxygen atom tends to stay on the surface forming oxide, whereas the carbon atoms penetrates the uranium lattice forming carbides. Thus an increase in the chemisorption energy for the interstitial site of carbon is noted as

compared to oxygen. This trend is also indicated in the most favorable site for chemisorption, as for oxygen the most favorable site is the bridge site with chemisorption energies of 7.887eV and 7.965eV for the non-spin and spin polarized cases, respectively, the adsorption distances being 1.19Å and 1.22Å for the same. For carbon, the most favorable site is the center site with chemisorption energies of 7.816eV and 7.895eV for the non-spin and spin polarized cases, respectively, the adsorption distances being 0.52Å and 0.62Å for the same, exhibiting its tendency to penetrate the lattice. In view of the above results of distance verses chemisorption energy, we conclude that in this case the site with highest coordination number, the center site with coordination number four, is the most favorable for carbon adsorption with bridge site with coordination number two and top site with coordination number one, being the other two favorable sites in that order. The interstitial site is the least favorable as its interaction with the top layer is considerably low.

Similar results are obtained for the spin polarized calculations. With the inclusion of spin polarization, the chemisorption energies are consistently higher than the non-spin polarized case, but the energies are comparable, whereas the adsorption distances differ slightly compared to the non-spin-polarized case. In this case also, the center site is the most favorable site for oxygen adsorption. For the spin-polarized case, the chemisorption energies for center, bridge, top and interstitial sites are 7.895eV, 6.559eV, 4.492eV, and 1.981eV and the adsorption distances are 0.52 Å, 1.14 Å, 1.88 Å, and 1.75 Å respectively. For the most favorable adsorption site, the center position, the chemisorption energy is higher by 0.079eV for the spin polarized case, compared to

the non-spin polarized case, which was also true for the oxygen adsorption where the two level of theories differed by 0.078eV for the most favorable bridge position. To study the effects of spin polarization, we also calculated the spin magnetic moments for different chemisorption sites of the carbon adatom (see Table 3.3). As mentioned earlier, the magnetic moments of the bare uranium layers drop rapidly as the number of layers increase from monolayer to 3-layer. After adsorption of carbon adatom on the U (100) surface, similar to the adsorption of oxygen adatom, the magnetic moment of the system as a whole reduces considerably. The bridge site has the highest magnetic moment of $0.301 \mu_B$ per atom, similar to the case of oxygen adsorption, where the bridge site had the highest magnetic moment. The top, center, and interstitial sites have a magnetic moment of $0.157\mu_B$, $0.086\mu_B$, and $0.024\mu_B$ per atom, respectively. Table 3.5 lists the Mulliken spin and charge distribution [89-91] for the most stable chemisorption site in the spin polarized case for the adsorption of carbon adatom, namely, the center site. As mentioned before, the charge distribution for the bare uranium layers show that in the first and the third layer all the atoms have negative charges, 0.079e each, while in the second layer all the atoms have positive charges, 0.158e each. After carbon adsorption, evidently, the carbon atom acquires negative charge, 0.712e, primarily from the first layer of uranium and all the atoms in the first layer are now positively charged. The charge distributions for second and the third layers changes, but not considerably, as the carbon adatom interacts mainly with atoms in the first layer of uranium. The change in charges in the second layer is higher than the changes in the charges in the third layer. For the bare uranium layers, analysis of the spin distribution shows that

spins of all the atoms are aligned in the same direction. After carbon adsorption, the spin of all the four atoms in the first layer are reversed, while in the second layer, spin of two of the atoms are reversed. For the third layer the spin of the atoms are unchanged, hence we can conclude that the effects of chemisorption of carbon is negligible in the third layer, but the spin and charge for the first two layers are affected considerably. Thus, the spin and charge distribution of the uranium slab changes notably after carbon adsorption, which can also be seen from the drop of magnetic moment, from $1.610\mu_B$ per atom for the bare uranium layers to $0.086\mu_B$ per atom for the carbon adsorbed center site. Also charge and spin distribution tables for other chemisorption sites, top, bridge and interstitial are given in Table 3.9, Table 3.10 and Table 3.11 respectively.

Analyzing the band energetics of the bare, oxygen-adsorbed, and carbonadsorbed uranium layers, we found that the band gaps did not change significantly for non-spin-polarized calculations compared to the spin-polarized calculations. As an example, the band gaps for uranium 6p and 5f bands without spin polarization is 14.806eV compared to 14.436eV with spin polarization. The Fermi level is seen to be formed, basically, by the 7*s* orbitals. For the oxygen-adsorbed layers, considering only the most favorable site for adsorption, namely the bridge site, the band gaps for the nonspin-polarized and the spin-polarized cases are 10.622eV and 10.519eV. Also there exists a band gap of 2.442eV with non-spin-polarization and 2.341eV with spinpolarization between the hybridized O 2p - U 5*f* band and the remaining U 5*f* electrons. For the carbon-adsorbed layers, considering only the most favorable site for adsorption, namely the center site, the band gaps for the non spin polarized and the spin polarized cases are 8.005eV and 7.906eV. Also there exists a band gap of 6.038eV with non-spinpolarization and 5.857eV with spin polarization between the hybridized C 2p - U 5fband and the remaining U 5f electrons. It can be inferred from the above data that after the adsorption of oxygen adatom, the band gap of uranium reduces considerably, and after the adsorption of carbon adatom the band gap reduces even further. The main reason for this reduction in the band gaps is due to the fact that the oxygen and carbon 2p orbitals hybridize with the lower end of uranium 5f orbitals and split the 5f band. This was also observed in our previous work, where it was seen that the bonding between the oxygen and the Pu atom is due to the hybridization of Pu 5f and O 2p orbitals. In figures 3.25-330, we have plotted 5f-DOS for uranium (100) bare surfaces and the most favorable oxygen and carbon chemisorbed surfaces at both non-spin polarized and spin polarized levels, respectively. A Gaussian broadening procedure has been employed here to compute the DOS[64-72]. A Gaussian $exp(-\alpha x^2)$ is assigned to each energy eigenvalue with $\alpha = 1000$, such that the width at the half height is 0.05eV. Up and down spins have been summed in drawing the DOS plots and the Fermi energy is normalized to zero. From the DOS for the bare uranium for the non-spin and spin polarized cases (Figs. 3.25-3.26), it is evident that some 5f electrons are delocalized, crossing the Fermi level and taking part in the chemical bonding process. From the DOS for both spin-polarized and non-spin-polarized oxygen and carbon adsorbed uranium surfaces (Figs. 3.27-3.30), we note that the hybridization between uranium 5forbitals and the oxygen 2p orbitals is very weak and the bonding is primarily ionic. On

the other hand, there is strong hybridization between C 2p and U 5f orbitals. Moreover the overall pattern of the DOS is affected by oxygen and carbon adsorption. Also after the adsorption of oxygen and carbon on the uranium (100) surface, the crossing of the Fermi level by the 5f electrons persists exhibiting itinerant behavior. Also, in general, work functions increase after oxygen and carbon adsorptions on a uranium surface. For the non-spin-polarized and spin-polarized oxygen adsorption, the increase in the values are 0.228eV and 0.219eV, respectively. For carbon, the corresponding values are 0.16eV and 0.14eV, respectively.

In conclusion, we have studied atomic oxygen and carbon adsorption on γ -uranium (100) surface using generalized gradient approximation to density functional theory with Perdew and Wang functional. For oxygen adsorption on U (100) surface, the bridge position is found to be the most favorable site for chemisorption for both non-spin and spin polarized cases. For carbon adsorption on U (100) surface, the center position is found to be the most favorable site for chemisorption for both non-spin and spin polarized cases. For carbon adsorption on U (100) surface, the center position is found to be the most favorable site for chemisorption for both non-spin and spin polarized cases. The coordination numbers are found to have a significant role in the adsorption process. The magnetic moments of the 3-layer uranium slab reduces significantly after oxygen and carbon adsorptions on any of the adsorption sites studied. Mulliken spin and charge distribution analysis indicates that the interaction of uranium with oxygen and carbon takes place, mainly in the first layer, as the spins and charges of the atoms in the first layer are changed considerably, with the second and third layer being only slightly affected. Finally, the band gaps of bare uranium layers were seen to

be reducing significantly upon the adsorption of oxygen and carbon, whereas the work functions are found to increase after oxygen and carbon adsorption.

Table 3.1 Oxygen chemisorption energies (in eV) and distances (in Å) for the non-spin polarized case for the U (100) surface. The corresponding results from our previous work for the Pu (100) surfaces are also shown.

Sites	U (100)		Pu (100)	
	C.E. in eV	r in Å	C.E. in eV	r in Å
Тор	7.237	1.86	6.470	1.83
Bridge	7.887	1.19	7.065	1.41
Center	7.658	0.66	7.386	0.92
Interstitial	0.879	1.73	5.422	2.14

Table 3.2 Oxygen chemisorption energies (in eV), distances (in Å), and magnetic moments in μ_B per atom for the spin-polarized case for the U (100) surface. The corresponding results from our previous work for the Pu (100) surfaces are also shown.

Sites	U (100)		Pu (100)		Magnetic moments	Magnetic moments
	C.E. in eV	r in Å	C.E. in eV	r in Å	in μ _B per atom for U (100)	in μ _B per atom for Pu (100)
Тор	7.261	1.86	4.682	1.85	0.158	1.56
Bridge	7.965	1.22	6.700	1.45	0.167	1.58
Center	7.797	0.64	7.080	1.02	0.021	1.65
Interstitial	0.926	1.71	4.936	2.14	0.008	1.92

	Uranium layers		Uranium + Oxygen layers
	Charge	Spin	Charge Spin
O atom	Х	Х	-0.618 0.057
1 st Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.0412.261-0.0422.2580.184-1.2700.185-1.312
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	$\begin{array}{cccc} 0.166 & 0.123 \\ 0.154 & 0.031 \\ 0.166 & 0.120 \\ 0.153 & 0.030 \end{array}$
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.073-2.238-0.074-2.238-0.0812.173-0.0802.176

Table 3.3 Spin and charge distributions of bare uranium layers and for most favorable chemisorption configuration for oxygen adatom (spin-polarized bridge site).

Table 3.4 Carbon chemisorption energies (in eV) and distances (in Å) for the non-	-spin
polarized and spin-polarized cases for the U (100) surface.	

Sites	Spin non-polarization		Spin-polarized		Magnetic moments
	C.E. in eV	r in Å	C.E. in eV	r in Å	in μ_B per atom
Тор	4.486	1.88	4.492	1.88	0.157
Bridge	6.551	1.13	6.559	1.14	0.301
Center	7.816	0.62	7.895	0.52	0.086
Interstitial	1.974	1.74	1.981	1.75	0.024

Table 3.5 Spin and charge distributions of bare uranium layers and for most favorable chemisorption configuration for carbon adatom (spin- polarized center site).

	Uranium layers		Uranium + Carbon layers
	Charge	Spin	Charge Spin
C atom	Х	Х	-0.712 -0.120
1 st Layer	-0.079	-2.054	0.087 1.973
5	-0.079	-2.054	0.145 1.998
	-0.079	-2.054	0.145 2.021
	-0.079	-2.054	0.086 1.996
2 nd Layer	0.158	-0.721	0.194 -0.206
	0.158	-0.721	0.106 0.032
	0.158	-0.721	0.108 0.259
	0.158	-0.721	-0.712 -0.206
3 rd Layer	-0.079	-2.054	-0.074 -2.224
-	-0.079	-2.054	-0.060 -2.207
	-0.079	-2.054	-0.059 -2.209
	-0.079	-2.054	-0.074 -2.225

	Uranium layers		Uranium + Oxygen layers
	Charge	Spin	Charge Spin
O atom	Х	Х	-0.476 0.010
1 st Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.0062.253-0.0382.1980.0732.1910.158-0.245
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	0.1320.0800.1320.0780.1330.0780.1340.075
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.073-2.238-0.084-2.131-0.042-2.103-0.1201.957

Table 3.6 Spin and charge distribution of bare uranium layers and spin polarized top site for the chemisorption of oxygen adatom.

	Uranium layers		Uranium + Oxygen layers
	Charge	Spin	Charge Spin
O atom	Х	Х	-0.730 -0.065
1 st Layer	-0.079	-2.054	0.086 2.183
2	-0.079	-2.054	0.138 2.186
	-0.079	-2.054	0.140 2.177
	-0.079	-2.054	0.089 2.174
2 nd Layer	0.158	-0.721	0.104 -0.078
2	0.158	-0.721	0.259 -0.068
	0.158	-0.721	0.094 0.245
	0.158	-0.721	0.104 -0.078
3 rd Laver	-0.079	-2.054	-0.075 -2.242
	-0.079	-2.054	-0.067 -2.233
	-0.079	-2.054	-0.067 -2.233
	-0.079	-2.054	-0.075 -2.242

Table 3.7 Spin and charge distribution of bare uranium layers and spin polarized center site for the chemisorption of oxygen adatom.

	Uranium layers		Uranium + Oxygen layers
	Charge	Spin	Charge Spin
O atom	Х	Х	-0.645 -0.001
1 st Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.111 2.387 -0.017 2.289 -0.117 2.289 0.028 1.482
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	$\begin{array}{cccc} 0.221 & 0.010 \\ 0.210 & 0.013 \\ 0.212 & 0.013 \\ 0.219 & 0.011 \end{array}$
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.108-2.396-0.019-2.277-0.019-2.2770.045-1.197

Table 3.8 Spin and charge distribution of bare uranium layers and spin polarized interstitial site for the chemisorption of oxygen adatom.

	Uranium layers		Uranium + Carbon layers
	Charge	Spin	Charge Spin
C atom	Х	Х	-0.339 -0.048
1 st Laver	-0.079	-2.054	0.019 2.285
J J	-0.079	-2.054	0.116 2.133
	-0.079	-2.054	0.116 2.133
	-0.079	-2.054	-0.077 -0.194
2 nd Laver	0.158	-0.721	0.112 0.096
5	0.158	-0.721	0.130 0.090
	0.158	-0.721	0.133 0.085
	0.158	-0.721	0.111 0.091
3 rd Laver	-0.079	-2.054	-0.081 -2.390
2 20,01	-0.079	-2.054	-0.063 -2.098
	-0.079	-2.054	-0.063 -2.098
	-0.079	-2.054	-0.115 1.958

Table 3.9 Spin and charge distribution of bare uranium layers and spin polarized top site for the chemisorption of carbon adatom.

	Uranium layers		Uranium + Carbon layers
	Charge	Spin	Charge Spin
C atom	Х	Х	-0.390 0.039
1 st Layer	-0.079	-2.054	-0.003 2.280
5	-0.079	-2.054	-0.002 2.281
	-0.079	-2.054	-0.017 -0.490
	-0.079	-2.054	-0.023 -0.461
2 nd Layer	0.158	-0.721	0.179 0.129
5	0.158	-0.721	0.194 0.184
	0.158	-0.721	0.179 0.097
	0.158	-0.721	0.197 0.165
3 rd Laver	-0 079	-2 054	-0.077 -2.262
	-0.079	-2.054	-0.077 -2.262
	-0.079	-2.054	-0.079 2.103
	-0.079	-2.054	-0.079 2.102

Table 3.10 Spin and charge distribution of bare uranium layers and spin polarized bridge site for the chemisorption of carbon adatom.

	Uranium layers		Uranium + Carbon layers
	Charge	Spin	Charge Spin
C atom	Х	Х	-0.652 -0.004
1 st Laver	-0.079	-2.054	-0.081 2.350
	-0.079	-2.054	-0.021 2.249
	-0.079	-2.054	-0.020 2.248
	-0.079	-2.054	-0.101 1.109
2 nd Laver	0.158	-0.721	0.262 0.019
5	0.158	-0.721	0.287 0.018
	0.158	-0.721	0.265 0.019
	0.158	-0.721	0.291 0.018
3 rd Laver	-0 079	-2.054	-0.080 -2.353
	-0.079	-2 054	-0.020 -2.238
	-0.079	-2.054	-0.019 -2.237
	-0.079	-2.054	-0.110 -0.896

Table 3.11 Spin and charge distribution of bare uranium layers and spin polarized interstitial site for the chemisorption of carbon adatom.



Figure 3.1 Oxygen adsorption on U (100) surface at top site: (a) Side view (b) Top view



Figure 3.2 Oxygen adsorption on U (100) surface at bridge site: (a) Side view (b) Top view



Figure 3.3 Oxygen adsorption on U (100) surface at center site: (a) Side view (b) Top view



Figure 3.4 Oxygen adsorption on U (100) surface at interstitial site: Side view



Figure 3.5 Carbon adsorption on U (100) surface at top site: (a) Side view (b) Top view



Figure 3.6 Carbon adsorption on U (100) surface at bridge site: (a) Side view (b) Top view



Figure 3.7 Carbon adsorption on U (100) surface at center site: (a) Side view (b) Top view



Figure 3.8 Carbon adsorption on U (100) surface at interstitial site: Side view



Figure 3.9 Non-spin-polarized chemisorption energy versus the oxygen adatom distance from the U (100) surface in the top position.



Figure 3.10 Spin-polarized chemisorption energy versus the oxygen adatom distance from the U (100) surface in the top position.



Figure 3.11 Non-spin-polarized chemisorption energy versus the oxygen adatom distance from the U (100) surface in the bridge position.



Figure 3.12 Spin-polarized chemisorption energy versus the oxygen adatom distance from the U (100) surface in the bridge position.



Figure 3.13 Non-spin-polarized chemisorption energy versus the oxygen adatom distance from the U (100) surface in the center position.



Figure 3.14 Spin-polarized chemisorption energy versus the oxygen adatom distance from the U (100) surface in the center position.



Figure 3.15 Non-spin-polarized chemisorption energy versus the oxygen adatom distance from the U (100) surface in the interstitial position.



Figure 3.16 Non-spin-polarized chemisorption energy versus the oxygen adatom distance from the U (100) surface in the interstitial position.


Figure 3.17 Non-spin-polarized chemisorption energy versus the carbon adatom distance from the U (100) surface in the top position.



Figure 3.18 Spin-polarized chemisorption energy versus the carbon adatom distance from the U (100) surface in the top position.



Figure 3.19 Non-spin-polarized chemisorption energy versus the carbon adatom distance from the U (100) surface in the bridge position.



Figure 3.20 Spin-polarized chemisorption energy versus the carbon adatom distance from the U (100) surface in the bridge position.



Figure 3.21 Non-spin-polarized chemisorption energy versus the carbon adatom distance from the U (100) surface in the center position.



Figure 3.22 Spin-polarized chemisorption energy versus the carbon adatom distance from the U (100) surface in the center position.



Figure 3.23 Non-spin-polarized chemisorption energy versus the carbon adatom distance from the U (100) surface in the interstitial position.



Figure 3.24 Spin-polarized chemisorption energy versus the carbon adatom distance from the U (100) surface in the interstitial position



Figure 3.25 Density of states for U 5*f* for the non-spin polarized (NSP) case for bare uranium. Fermi energy is normalized to zero.



Figure 3.26 Density of states for U 5f for the spin polarized (SP) case for bare uranium. Fermi energy is normalized to zero.



Figure 3.27 Density of states for U 5f + O 2p for the non-spin polarized (NSP) case for bridge position. Fermi energy is normalized to zero.



Figure 3.28 Density of states for U 5f + O 2p for the spin polarized (SP) case for bridge position. Fermi energy is normalized to zero.



Figure 3.29 Density of states for U 5f + C 2p for the non-spin polarized (NSP) case for the center position. Fermi energy is normalized to zero.



Figure 3.30 Density of states for U 5f + C 2p for the spin polarized (SP) case for the center position. Fermi energy is normalized to zero.



Figure 3.31 Spin arrangements (spins in Bohr magnetons) within the unit cell (a) bare U (100) surface (b) oxygen and (c) carbon adsorbed U(100) surface for the most favorable chemisorption position.

CHAPTER 4

ADSORPTION OF CO MOLECULE ON (100) SURFACE OF γ-URANIUM 4.1 Molecular adsorption of CO molecule on U (100) surface

To study CO adsorption on the γ -uranium (100) surface, we modeled the surface with three layers of uranium at the experimental lattice constant. 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.[32] Also, recently, Ray and Boettger showed in a study of quantum size effects of δ -plutonium surface that surface energies converge within the first three layers.[33] 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 different symmetrical approaches: i) directly on top of a U atom (top position); ii) in the middle of two nearest neighbor U atoms (bridge position); iii) in the center of the smallest unit structures of the surfaces (*center* position). As the smallest structure of the (100) γ -uranium surface is a square, these three sites are the only symmetrically distinguishable sites. Again, for each of these positions we consider several approaches of chemisorption. They are: 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 condition, 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 oxygen atom of CO 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 chemisorption energies are 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 chemisorption energies both of these energies are spin polarized. E(CO) is the energy of the oxygen molecule in the singlet state in both cases. The chemisorption energies as a function of the separation distance of the CO molecule from the top layer for four different approaches, including non-spin-polarized (NSP) and spin-polarized (SP) cases, are shown in Fig.(4.7 - 4.30). The chemisorption energies and the corresponding distances for the non-spin polarized and spin polarized cases are given in Table 4.1 and 4.2 respectively. The distances r given in the table are measured as the distance from the uranium surface to the oxygen or carbon atoms, if both the oxygen and carbon 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.

We start by describing the chemisorption process of CO at different sites on uranium surfaces. Consider first the top sites without spin polarization (Fig.4.1 and 4.2). We have already mentioned that there are four different approaches for each site. For the two vertical approaches, Vert1 and Vert2, the chemisorption distances from the uranium surface to the CO molecule are 2.987Å and 2.447Å, whereas the chemisorption energies are 0.0781eV and 0.9328eV respectively. Vert1 is one of the least favorable approaches for chemisorption showing that the adsorption of CO molecule with O atom facing the surface is really not feasible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances from the uranium surface to the CO molecule are 2.792Å and 2.839Å, whereas the chemisorption energies are 0.2091eV and 0.1821eV respectively. Both approaches, Hor1 and Hor2, are seen to have almost similar chemisorption distances as well as chemisorption energies, showing that both the approaches are equally probable. For the above top sites with different approaches, even after inclusion of spin polarization, the chemisorption distances and chemisorption energies were not found to change considerably. For the two vertical approaches, vert1 and vert2, the chemisorption distances from the uranium surface to the CO molecule are 3.121Å and 2.454Å, whereas the chemisorption energies are 0.1776eV and 0.9968eV respectively. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances from the uranium surface to the CO molecule are 2.792Å and 2.941Å, whereas the chemisorption energies are 0.2951eV and 0.2665eV respectively. It can be seen that the change in chemisorption energy due to the inclusion of spin polarization is very small. The magnetic moments per atom for the four approaches on the top site are $0.0058\mu_B$, $0.0355\mu_B$, $0.0089\mu_B$ and $0.0061\mu_B$ for Vert1, Vert2, Hor1 and Hor2 approaches respectively. For the bare uranium layers the magnetic moment was found to be $1.610\mu_B$ per atom. Thus it can be said that the magnetic moment of bare uranium layers drops rapidly after the adsorption of CO molecule on the top site.

We now discuss the chemisorption of CO molecule on the bridge site with different approaches (Fig. 4.3 and 4.4). For the non-spin polarization case, the two vertical approaches, Vert1 and Vert2, the chemisorption distances from the uranium surface to the CO molecule are 2.701Å and 1.883Å, whereas the chemisorption energies are 0.6812eV and 1.0818eV respectively. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances from the uranium surface to the CO molecule are 2.263Å and 2.334Å, whereas the chemisorption energies are 0.4107eV and 0.2999eV respectively. Both approaches, Hor1 and Hor2, are seen to have almost similar chemisorption distances as well as chemisorption energies, showing that both the approaches are equally probable. For the above bridge sites with different approaches, even after inclusion of spin polarization, the chemisorption distances and chemisorption energies were not found to change considerably. For the two vertical approaches, vert1 and vert2, the chemisorption distances from the uranium surface to the CO molecule are 2.706Å and 1.881Å, whereas the chemisorption energies are 0.7888eV and 1.1134eV respectively. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances from the uranium surface to the CO molecule are 2.263Å and 2.334Å, whereas the chemisorption energies are 0.5169eV and 0.3098eV respectively. It can be seen that the change in chemisorption energy due to the inclusion of spin polarization is very small. The magnetic moments per atom for the four approaches on the bridge site are $0.0004\mu_B$, $0.0282\mu_B$, $0.0157\mu_B$ and $0.0121\mu_B$ for Vert1, Vert2, Hor1 and Hor2 approaches respectively.

We now discuss the chemisorption of CO molecule on the center site with different approaches (Fig. 4.5 and 4.6). For the non-spin polarization case, the two vertical approaches, Vert1 and Vert2, the chemisorption distances from the uranium surface to the CO molecule are 3.016Å and 0.665Å, whereas the chemisorption energies are 0.0474eV and 1.3411eV respectively. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances from the uranium surface to the CO molecule are 0.695Å and 0.705Å, whereas the chemisorption energies are 0.3217eV and 1.2332eV respectively. In this case for the center position, both approaches, Horl and Hor2, are seen to have almost similar chemisorption distances but the chemisorption energies are considerably different showing that Hor2 approach is far more favorable compared to Hor1 which was not true for the top and the bridge, where both the approaches were almost equally probable. For the above bridge sites with different approaches, even after inclusion of spin polarization, the chemisorption distances and chemisorption energies were not found to change considerably. For the two vertical approaches, vert1 and vert2, the chemisorption distances from the uranium surface to the CO molecule are 3.016Å and 0.665Å, whereas the chemisorption energies are 0.0586eV and 1.3558eV respectively. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances from the uranium surface to the CO molecule are 0.695Å and 0.692Å, whereas the chemisorption energies are 0.3411eV and 0.1.2447eV respectively. It can be seen that the change in chemisorption energy due to the inclusion of spin polarization is very small. The magnetic moments per atom for the four approaches on the center site are $0.0271\mu_B$, $0.3399\mu_B$, $0.0781\mu_B$ and $0.0679\mu_B$ for Vert1, Vert2, Hor1 and Hor2 approaches respectively. It can be seen that the center position with Vert2 approach is the most favorable of all the sites with different approaches. Also, the configuration in which CO molecule is very close to the uranium surface is found to be particularly more stable, as can be seen from the chemisorption distance of 0.665Å for the center site with Vert2 approach. In figures 4.31-4.32, we have plotted 5f + CO 2p DOS for center position with Vert2 approach at both non-spin polarized and spin polarized levels, respectively. A Gaussian broadening procedure has been employed here to compute the DOS[64-72]. A Gaussian exp($-\alpha x^2$) is assigned to each energy eigenvalue with $\alpha =$ 1000, such that the width at the half height is 0.05eV. Up and down spins have been summed in drawing the DOS plots and the Fermi energy is normalized to zero. From the DOS for the bare uranium for the non-spin and spin polarized cases (Figs. 3.25-3.26), it is evident that some 5f electrons are delocalized, crossing the Fermi level and taking part in the chemical bonding process. From the DOS for both spin-polarized and non-spin-polarized CO adsorbed uranium surfaces (Figs. 4.31-4.32), we note that the hybridization between uranium 5f orbitals and the CO 2p orbitals is very weak and the bonding is primarily ionic. Moreover the overall pattern of the DOS is affected by CO adsorption. Also after the adsorption of CO molecule on the uranium (100) surface, the crossing of the Fermi level by the 5*f* electrons persists exhibiting itinerant behavior. 4.2 *Dissociative adsorption of CO molecule on U (100) surface*

To investigate the possibility of the CO molecule being dissociated on the uranium surface, we optimized the distances of the carbon and oxygen atom from the surface (r_d) and the distance between the two atoms (r_o), carbon and oxygen, simultaneously. In this section we discuss the results for the non-spin polarized level of theory. For the non-spin polarized case, both *E* (U-layers + CO) and *E* (U-layers) were calculated without spin polarization. *E* (CO) is the energy of the CO molecule in the singlet state. The chemisorption energies, and the corresponding distances, are given in Table 4.15. The distances r_d given in the table are measured as the distance from the uranium surface to the carbon and oxygen atoms, if both the carbon and oxygen atoms are at the same height, or to the nearer of the two atoms if one of them is closer to the surface than the other.

We start by describing the chemisorption process of CO at the different sites on uranium surface. Consider first the top sites for the non-spin polarized case (Fig4.1 and 4.2). For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to CO are 2.817Å and 2.342Å; while the chemisorption energies are 0.9148eV and 2.7037eV respectively. In the Vert1 and Vert2 approaches, the distance between the carbon and oxygen atoms (r_o) is 1.146Å and 1.139Å respectively, which implies that the dissociation of CO molecule is not feasible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances (r_d) from the uranium surface to CO are 2.611Å and 2.785Å; while the chemisorption energies are 1.6548eV and 2.9306eV respectively. In the Hor1 and Hor2 approaches, the distance between the carbon and oxygen atoms (r_o) is stretched to1.335Å and 1.310Å respectively, which is slightly higher than the Vert1 and Vert2 approaches, but not high enough to consider the CO molecule being dissociated. It can be seen that for the various approaches on the top site, Hor2 is the most favorable while Vert1 is found to be the least favorable among the four approaches.

Now we consider the four different approaches on the bridge site (Fig2). For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to CO are 2.670Å and 1.589Å; while the chemisorption energies are 1.1036eV and 2.9315eV respectively. It can be seen that for Vert2 approach, the distance from the uranium surface is less compared to the Vert2 approach for the top site. In the Vert1 and Vert2 approaches, the distance between the carbon and oxygen atoms (r_0) is 1.129Å and 1.134Å respectively, which implies that the dissociation of CO molecule is not feasible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances (r_d) from the uranium surface to CO are 1.782Å and 1.989Å; while the chemisorption energies are 2.1765eV and 1.7505eV respectively. In the Hor1 and Hor2 approaches, the distance between the carbon and oxygen atoms (r_0) is stretched to1.357Å and 1.411Å respectively, which is slightly higher than the Vert1 and Vert2 approaches, but not high enough to consider the CO molecule being dissociated. Similar to the case for top site, the Vert1 approach is the least favorable. But for the bridge site, Vert2 approach is the most favorable which was not true for top site.

Now we consider the four different approaches on the center site (Fig.4.3 and 4.4). For the two vertical approaches, Vert1 and Vert2, the chemisorption distances (r_d) from the uranium surface to CO are 0.789Å and 0.613Å; while the chemisorption energies are 1.1914eV and 2.9298eV respectively. It can be seen that for Vert2 approach, the distance from the uranium surface is less compared to the Vert2 approach for the top and the bridge site. In the Vert1 and Vert2 approaches, the distance between the carbon and oxygen atoms (r_0) is 1.142Å and 1.311Å respectively, which implies that the dissociation of CO molecule is not feasible. For the two horizontal approaches, Hor1 and Hor2, the chemisorption distances (r_d) from the uranium surface to CO are 0.711Å and 0.774Å; while the chemisorption energies are 2.7599eV and 2.5439eV respectively. In the Hor1 and Hor2 approaches, the distance between the carbon and oxygen atoms (r_0) is stretched to 1.319Å and 1.427Å respectively, which is slightly higher than the Vert1 and Vert2 approaches, but not high enough to consider the CO molecule being dissociated. Similar to the case for top and bridge site, the Vert1 approach is the least favorable while Vert2 is found to be the most favorable approach.

		-	
Sites	Approach	r in A	C.E. in eV
Тор	Vert 1	2.987	0.0781
	Vert 2	2.447	0.9328
	Hor 1	2.792	0.2091
	Hor 2	2.839	0.1821
Bridge	Vert 1	2.701	0.6812
	Vert 2	1.883	1.0818
	Hor 1	2.263	0.4107
	Hor 2	2.334	0.2999
Center	Vert 1	3.016	0.0474
	Vert 2	0.665	1.3411
	Hor 1	0.695	0.3217
	Hor 2	0.705	1.2332

Table 4.1 Chemisorption energies (C.E.) in eV for different sites and approaches with adsorption distances (r) in Å from the uranium surface for the non-spin polarized case.

Non-spin polarized

* There are four approaches:

(i) CO molecule approaches vertically to the surface with O on the lower end – Vert 1

(ii) CO molecule approaches vertically to the surface with C on the lower end – Vert 2

(iii) CO molecule parallel to the surface and parallel to the bcc lattice vectors – Hor 1

(iv) CO molecule parallel to the surface and having an angle 45° with the bcc lattice vectors – Hor 2

		Spin polarized	d	
Sites	Approach	r in A	C.E. in eV	Magnetic moments in µ _B per atom
Тор	Vert 1	3.121	0.1776	0.0058
	Vert 2	2.454	0.9968	0.0355
	Hor 1	2.792	0.2951	0.0089
	Hor 2	2.941	0.2665	0.0061
Bridge	Vert 1	2.706	0.7888	0.0004
	Vert 2	1.881	1.1134	0.0282
	Hor 1	2.263	0.5169	0.0157
	Hor 2	2.334	0.3098	0.0231
Center	Vert 1	3.016	0.0586	0.0004
	Vert 2	0.665	1.3558	0.3399
	Hor 1	0.695	0.3411	0.0159
	Hor 2	0.692	1.2447	0.0284

Table 4.2 Chemisorption energies (C.E.) in eV for different sites and approaches with adsorption distances (r) in Å from the uranium surface for the spin polarized case.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom	Х	Х	0.049 -0.014
O atom	Х	Х	-0.120 0.000
1 st Layer	-0.079 -0.079	-2.054 -2.054	-0.070 2.350 -0.091 2.112
	-0.079 -0.079	-2.054 -2.054	-0.091 2.112 0.042 -2.075
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	$\begin{array}{cccc} 0.146 & 0.013 \\ 0.147 & 0.013 \\ 0.146 & 0.012 \\ 0.146 & 0.012 \end{array}$
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.063-2.347-0.071-2.104-0.071-2.104-0.0992.101

Table 4.3 Spin and charge distribution of bare uranium layers and spin polarized top site with Vert1 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom	Х	Х	-0.032 -0.073
O atom	Х	Х	-0.156 -0.043
1 st Laver	-0.079	-2.054	-0.037 2.338
5	-0.079	-2.054	-0.013 2.120
	-0.079	-2.054	-0.013 2.120
	-0.079	-2.054	-0.072 -1.787
2 nd Laver	0.158	-0.721	0.127 0.064
,	0.158	-0 721	0.126 0.063
	0 158	-0 721	0.126 0.063
	0.158	-0.721	0.125 0.062
3 rd Laver	-0 079	-2.054	-0.063 -2.354
5 Euger	-0.079	-2 054	-0 070 -2 084
	-0.079	-2 054	-0.070 -2.084
	-0.079	-2.054	-0.122 2.091

Table 4.4 Spin and charge distribution of bare uranium layers and spin polarized top site with Vert2 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom	Х	Х	-0.010 -0.091
O atom	Х	Х	-0.169 -0.020
1 st Layer	-0.079	-2.054	-0.046 2.342
-	-0.079	-2.054	0.022 2.117
	-0.079	-2.054	-0.061 2.114
	-0.079	-2.054	0.056 -2.019
2 nd Layer	0.158	-0.721	0 133 0 040
5	0.158	-0.721	0.137 0.033
	0.158	-0.721	0.129 0.021
	0.158	-0.721	0.130 0.028
3 rd Laver	-0.079	-2.054	-0 070 -2 345
	-0.079	-2.054	-0.076 -2.095
	-0 079	-2 054	-0.076 -2.093
	-0.079	-2.054	-0.081 2.093

Table 4.5 Spin and charge distribution of bare uranium layers and spin polarized top site with Hor1 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom	Х	Х	0.012 -0.054
O atom	Х	Х	-0.158 -0.012
1 st Layer	-0.079	-2.054	-0.048 2.343
2	-0.079	-2.054	-0.039 2.106
	-0.079	-2.054	-0.029 2.105
	-0.079	-2.054	0.044 -2.045
2 nd Layer	0.158	-0.721	0.124 0.043
5	0.158	-0.721	0.137 -0.001
	0.158	-0.721	0.138 -0.002
	0.158	-0.721	0.135 0.044
3 rd Laver	-0.079	-2.054	-0.063 -2.346
	-0 079	-2 054	-0.072 -2.097
	-0 079	-2 054	-0 072 -2 096
	-0.079	-2.054	-0.109 2.096

Table 4.6 Spin and charge distribution of bare uranium layers and spin polarized top site with Hor2 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers	
	Charge	Spin	Charge Spin	_
C atom	Х	Х	0.071 0.000	
O atom	Х	Х	-0.115 0.000	
1 st Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	$\begin{array}{rrrr} -0.077 & 2.350 \\ -0.081 & 2.106 \\ -0.045 & 2.106 \\ -0.040 & -2.101 \end{array}$	
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.067-2.350-0.071-2.106-0.075-2.107-0.0852.100	

Table 4.7 Spin and charge distribution of bare uranium layers and spin polarized bridge site with Vert1 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom	X	X	-0.137 -0.005 -0.178 -0.007
O atom	Λ	Λ	
1 st Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.0422.349-0.0322.1570.0891.9550.076-1.656
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	$\begin{array}{cccc} 0.139 & 0.001 \\ 0.124 & 0.062 \\ 0.139 & 0.001 \\ 0.125 & 0.058 \end{array}$
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.068-2.367-0.071-2.123-0.074-2.078-0.0902.048

Table 4.8 Spin and charge distribution of bare uranium layers and spin polarized bridge site with Vert2 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom	Х	Х	-0.096 -0.142
O atom	Х	Х	-0.216 -0.055
1 st Layer	-0.079	-2.054	-0.039 2.330
5	-0.079	-2.054	-0.038 2.108
	-0.079	-2.054	0.157 1.869
	-0.079	-2.054	0.061 -1.989
2 nd Laver	0.158	-0.721	0.131 0.013
	0 158	-0 721	0.119 0.020
	0 158	-0 721	0.130 0.014
	0.158	-0.721	0.119 0.020
3 rd Laver	-0 079	-2 054	-0.067 -2.349
	-0.079	-2.054	-0.065 -2.087
	-0.079	-2.054	-0.089 -2.059
	-0.079	-2.054	-0.106 2.088

Table 4.9 Spin and charge distribution of bare uranium layers and spin polarized bridge site with Hor1 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers	
	Charge	Spin	Charge Spin	
C atom O atom	X X	X X	-0.078 -0.147 -0.346 -0.469	
1 st Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.0382.341-0.0572.1430.1451.9100.078-1.899	
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	$\begin{array}{cccc} 0.136 & 0.018 \\ 0.121 & 0.023 \\ 0.128 & 0.009 \\ 0.121 & 0.034 \end{array}$	
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.070-2.359-0.076-2.098-0.076-1.878-0.0812.048	

Table 4.10 Spin and charge distribution of bare uranium layers and spin polarized bridge site with Hor2 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom O atom	X X	X X	0.083 0.000 -0.115 0.000
1 st Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.0572.348-0.0622.105-0.0622.105-0.072-2.101
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.068-2.350-0.072-2.106-0.072-2.106-0.0802.100

Table 4.11 Spin and charge distribution of bare uranium layers and spin polarized center site with Vert1 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers	
	Charge	Spin	Charge Spin	
C atom O atom	X X	X X	-0.370 -0.031 -0.343 0.019	
1 st Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	
2 nd Layer	0.158 0.158 0.158 0.158	-0.721 -0.721 -0.721 -0.721	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	
3 rd Layer	-0.079 -0.079 -0.079 -0.079	-2.054 -2.054 -2.054 -2.054	-0.070-2.320-0.076-2.073-0.076-2.071-0.081-1.820	

Table 4.12 Spin and charge distribution of bare uranium layers and spin polarized center site with Vert2 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom	Х	Х	-0.113 -0.147
O atom	Х	Х	-0.289 -0.078
1 st Layer	-0.079	-2.054	-0.299 2.321
	-0.079	-2.054	-0.045 2.113
	-0.079	-2.054	0.145 1.898
	-0.079	-2.054	0.067 -1.970
2 nd Laver	0.158	-0.721	0.142 0.015
	0.158	-0.721	0.118 0.034
	0.158	-0.721	0.137 0.008
	0.158	-0.721	0.118 0.014
3 rd Layer	-0.079	-2.054	-0.068 -2.351
	-0 079	-2 054	-0.071 -2.069
	-0 079	-2 054	-0 079 -2 067
	-0.079	-2.054	-0.098 2.056

Table 4.13 Spin and charge distribution of bare uranium layers and spin polarized center site with Hor1 approach for the chemisorption of CO molecule.

	Uranium layers		Uranium + CO layers
	Charge	Spin	Charge Spin
C atom	X	X	-0.134 -0.156
O atom	X	X	-0.256 -0.457
1 st Layer	-0.079	-2.054	-0.057 2.334
	-0.079	-2.054	-0.057 2.145
	-0.079	-2.054	0.145 1.899
	-0.079	-2.054	0.067 -1.960
2 nd Laver	0.158	-0.721	0.142 0.014
5	0.158	-0.721	0.121 0.028
	0.158	-0.721	0.122 0.026
	0.158	-0.721	0.121 0.159
3 rd Layer	-0.079	-2.054	-0.070 -2.343
	-0.079	-2.054	-0.076 -2.067
	-0.079	-2.054	-0.076 -2.078
	-0.079	-2.054	-0.081 2.059

Table 4.14 Spin and charge distribution of bare uranium layers and spin polarized center site with Hor2 approach for the chemisorption of CO molecule.

Sites	Approach	r _d in Å	r_o in Å	C.E. in eV	
Тор	Vert 1	2.817	1.146	0.9148	
	Vert 2	2.342	1.139	2.7037	
	Hor 1	2.611	1.335	1.6548	
	Hor 2	2.785	1.310	2.9306	
Bridge	Vert 1	2.670	1.129	1.1036	
	Vert 2	1.589	1.134	2.9315	
	Hor 1	1.782	1.357	2.1765	
	Hor 2	1.989	1.411	1.7505	
Center	Vert 1	0.789	1.142	1.1914	
	Vert 2	0 613	1 311	2 9298	
	Hor 1	0.711	1 310	2 7599	
		0.711	1.019	2.7399	
		0.774	1.427	2.0439	

Table 4.15 Chemisorption energies (C.E.) 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.

Non-spin polarized

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 – Vert 1
(ii) CO molecule approaches vertically to the surface with C on the lower end – Vert 2
(iii) CO molecule parallel to the surface and parallel to the bcc lattice vectors – Hor 1
(iv) CO molecule parallel to the surface and having an angle 45° with the bcc lattice vectors – Hor 2





Figure 4.1 CO adsorption on U (100) surface at top site with vert1 approach: (a) Side view (b) Top view and vert2 approach: (c) Side view (d) Top view



Figure 4.2 CO adsorption on U (100) surface at top site with Hor1 approach: (a) Side view (b) Top view and Hor2 approach: (c) Side view (d) Top view



Figure 4.3 CO adsorption on U (100) surface at bridge site with Vert1 approach: (a) Side view (b) Top view and Vert2 approach: (c) Side view (d) Top view





Figure 4.4 CO adsorption on U (100) surface at bridge site with Hor1 approach: (a) Side view (b) Top view and Hor2 approach: (c) Side view (d) Top view


Figure 4.5 CO adsorption on U (100) surface at center site with Vert1 approach: (a) Side view (b) Top view and Vert2 approach: (c) Side view (d) Top view





Figure 4.6 CO adsorption on U (100) surface at center site with Hor1 approach: (a) Side view (b) Top view and Hor2 approach: (c) Side view (d) Top view



Figure 4.7 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the top position for the Vert1 approach.



Figure 4.8 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the top position for Vert1 approach.



Figure 4.9 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the top position for the Vert2 approach.



Figure 4.10 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the top position for the Vert2 approach.



Figure 4.11 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the top position for the Hor1 approach.



Figure 4.12 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the top position for the Hor1 approach.



Figure 4.13 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the top position for the Hor2 approach.



Figure 4.14 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the top position for the Hor2 approach.



Figure 4.15 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the bridge position for the Vert1 approach.



Figure 4.16 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the bridge position for the Vert1 approach.



Figure 4.17 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the bridge position for the Vert2 approach.



Figure 4.18 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the bridge position for the Vert2 approach.



Figure 4.19 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the bridge position for the Hor1 approach.







Figure 4.21 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the bridge position for the Hor2 approach.







Figure 4.23 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the center position for the Vert1 approach.



Figure 4.24 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the center position for the Vert1 approach.



Figure 4.25 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the center position for the Vert2 approach.



Figure 4.26 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the center position for the Vert2 approach.



Figure 4.27 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the center position for the Hor1 approach.



Figure 4.28 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the center position for the Hor1 approach.



Figure 4.29 Non-spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the center position for the Hor2 approach.



Figure 4.30 Spin-polarized chemisorption energy versus the CO molecule distance from the U (100) surface in the center position for the Hor2 approach.



Figure 4.31 Density of states for U 5f + CO 2p for the non-spin polarized (NSP) case for the center position, Vert2 approach. Fermi energy is normalized to zero.





CHAPTER 5

CONCLUSIONS

In conclusion, we have studied atomic oxygen and carbon adsorption on γ uranium (100) surface using generalized gradient approximation to density functional theory with Perdew and Wang functional. For oxygen adsorption on U (100) surface, the bridge position is found to be the most favorable site for chemisorption for both non-spin and spin polarized cases. For carbon adsorption on U (100) surface, the center position is found to be the most favorable site for chemisorption for both non-spin and spin polarized cases. The coordination numbers are found to have a significant role in the adsorption process. The magnetic moments of the 3-layer uranium slab reduces significantly after oxygen and carbon adsorptions on any of the adsorption sites studied. Mulliken spin and charge distribution analysis indicates that the interaction of uranium with oxygen and carbon takes place, mainly in the first layer, as the spins and charges of the atoms in the first layer are changed considerably, with the second and third layer being only slightly affected. Finally, the band gaps of bare uranium layers were seen to be reducing significantly upon the adsorption of oxygen and carbon, whereas the work functions are found to increase after oxygen and carbon adsorption.

We also studied the molecular adsorption of CO molecule at both, the non-spin polarized and spin polarized level of theories. It was seen that for the molecular adsorption of CO, center site with Vert2 approach was the most favorable. Inclusion of spin polarization did not have a significant effect on the chemisorption energies. All spin and charge distribution for all the sites was studied. It was found that the spins and charges of the first and second layer of the uranium slab are affected considerably, with the third layer being affected only slightly. Density of states for the most favorable chemisorption position showed that after the CO adsorption the overall pattern of the density of states changed compared to the bare uranium. We also studied the dissociative adsorption of CO molecule at the non-spin polarized level of theory. It was found that bridge site with Vert2 approach was the most favorable for chemisorption. Also dissociation of CO molecule was not found on any of the various studied chemisorption sites.

Future work on actinides would be really interesting. In particular, γ -uranium (100) surface can be used to do further calculations on the adsorption of carbon dioxide. Also (111) and (110) surfaces of γ -uranium can be used to study the adsorption of atomic oxygen and carbon adsorption, as well as adsorption of carbon monoxide and carbon dioxide.

APPENDIX A

A DENSITY FUNCTIOAL STUDY OF CHARGE STATE EFFECTS ON THE USE OF $Ag_2^-,\,Ag_2^+$ and Ag_2 for catalytic oxidation of

Introduction:

Clusters are not like solids; they are distinctly different from solids due to large surface to volume ratio. On the other hand, as the number of atoms increases, clusters tend to assume the properties of solid. Growing interest in the stabilities of small clusters and the evolution of bulk properties from cluster properties is also due to the emergence of a new science called nanoscience and its potential in industrial applications. In a way, "Clusters are aggregates of atoms and molecules, generally intermediate in size, between individual atoms and aggregates large enough to be called bulk matter". In definition, there is not lower or upper limit mentioned on the number of atoms that can be called a cluster. However in current literatures, there are tendencies to include dimers as clusters. For a fixed number of atoms of an element, a cluster can have several distinct geometrical structures which lead to different electronic distributions. This in turn produces different characteristic electronic states. Thus a 'spectrum' of clusters can be found with their own characteristic properties for any element. This makes the study of clusters interesting. Clusters are also known for producing new material. As for the reasons stated above, there is always a possibility to come up with a different combination of atoms having entirely new physical properties. The discovery of C_{60} is one of such events. After the discovery of this highly stable cluster, an entirely new field has opened up to study larger carbon clusters.

In the study of clusters, metal clusters have played important roles from the very beginning. The study of coinage metal clusters has taken a central role in this area due to their large scale usage in industry and also because they offer a wide range of characteristic properties. In terms of electronic complexity, coinage metals fall in between the alkali metals and transition metals that have partially filled *d*-electrons. Thus a study of coinage metals is a first step towards the exploration of more complex elements. In metal clusters, silver has received particular attention because of two reasons: one is that silver has d-electrons at the outer orbitals, overlapped by the partially filles s-orbitals, which makes the study of silver clusters interesting and challenging; the second one is its importance in photographic and catalytic processes. Hence a scientific understanding of pure silver and doped silver clusters is essential. Also small gold, silver and copper clusters are used extensively for catalytic processes. Also, though silver is a metal, small silver clusters are like insulators with high HOMO-LUMO gap (gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital). Moreover a lot of research is carried on to find an alternative way to make the automotive and other industrial exhaust pollution free. A major ingredient of this exhaust is carbon monoxide, and to decrease its content in these exhausts is one of the main goals of many research laboratories. Theoretically, we have tried to show that silver clusters can be used as a catalyst for the oxidation of carbon monoxide, and in the end, carbon dioxide is released in the air, which is less harmful to the environment.

As is well known, small clusters behave differently from corresponding bulk materials in many aspects such as chemical reactivity and catalytic properties. One of the typical examples is gold clusters.[92] Chemically inert in its bulk phase, nano-scale gold particles dispersed on metal oxide surfaces including TiO₂,[93, 94] MgO,[92,95]

and $Mg(OH)_2[96]$ have been found to facilitate a wide range of oxidation reactions, in particular the low temperature CO combustion. Studies have shown that the reactivity of gold clusters critically depend on the cluster size[94-96] and the stoichiometry[95, 97, 98] of the metal oxide substrate, which suggests that charge transfer between gold clusters and the substrate surface is partially responsible for the catalytic CO oxidation. Reactivity of free gold clusters and its size and charge state dependence have also been investigated experimentally[99-102] and theoretically.[102-105] Using local-spindensity molecular dynamics method[106] including generalized gradient corrections (GGA)[107], with nonlocal norm-conserving pseudopotentials for the $5d^{10}6s^1$, $2s^22p^2$, and 2s²2p⁴ valence electrons of Au, C, and O atoms, respectively, Häkkinen and Landman[103] studied the energetics and mechanism of O₂ and CO adsorption on Au₂⁻ and predicted catalytic reaction path of the CO oxidation by Au₂⁻ in presence of O₂. For bonding in gold clusters, they used a scalar-relativistic pseudopotential.[108-109] The theoretically predicted catalytic reaction cycle and a meta-stable intermediate carbonate complex Au₂CO₃⁻ were identified by temperature-dependent rf-ion trap mass measurements.[102]

This work is a natural extension of the remarkable catalytic reactivity exhibited in small gold clusters to an investigation of the chemical properties of small free silver clusters. Silver, also a noble metal, lies above gold in the same column of the periodic table. It has a fully occupied d shell and an unpaired outer s electron, very similar to gold. Therefore it is natural to expect that silver clusters, significantly less expensive then gold, are probable candidates for catalytic oxidation. Though much effort has been devoted in the research of the fascinating odd-even size alternation of the electronic properties of silver clusters in the nanoscale regime [110-114] less is known about the chemical reactivity of free silver clusters although supported silver clusters have been commercially used in ethylene oxidation processes.[115] Interaction of charged silver clusters with molecular oxygen have recently been studied in a number of experiments.[116-118] In particular, based on temperature-dependent measurements of the reaction kinetics under multi-collision conditions, Socaciu et al.[116] detected $\mathrm{Ag_2O}^+$ formed after molecular adsorption and dissociation of O_2. Mass spectra and kinetic measurements conducted by Hagen et al.[117] revealed an unprecedented size dependence in the adsorption of multiple molecules onto anionic silver clusters Ag n (n=1, 5). Ag $_{n}$ with odd n were found to adsorb two oxygen molecules, while Ag $_{n}$ with even n were found to adsorb one O_2 . Further investigation of reactions of negatively charged free silver clusters Ag_n with O₂, CO and mixture conducted by the same group indicated the catalytic activity of certain studied cluster sizes (n=7, 9, 11) in the CO oxidation. Co-adsorption complexes Ag n(CO)O2 were also detected for cluster sizes n = 4 and 6. These investigations indicate that small charged silver clusters can also be used as a catalyst in the CO combustion. In this work, we apply the generalized gradient approximation to density functional theory (GGA-DFT) [107, 119] to study the adsorption of CO, O2 and their mixture on anionic silver dimer Ag2, cationic silver dimer Ag2⁺, and neutral silver dimer Ag2, as well as the mechanism and reaction path of the possible catalytic CO oxidation on Ag_2^- , Ag_2^+ , and Ag_2 . In particular, we have investigated the catalytic cycle yielding 2 CO_2 molecules using Ag_2^- , Ag_2^+ , and Ag_2 as

catalysts. The catalytic cycles are given in scheme 1, 2 and 3 for Ag_2^- , Ag_2^+ , and Ag_2 respectively. This cycle is the same cycle studied by Häkkinen and Landman[103] for reactions with Au_2^- . In the section below, we outline the computational method followed by a discussion of our results.

Computational method and discussion of results:

In an *ab initio* calculations of the type reported here, there are two primary considerations: the choice of the basis set and the form of the exchange-correlation functionals. For carbon and oxygen, we have used a large all electron 6-311++G** [120-122] basis set, and, for silver, we have used a pseudopotential and an associated basis set.[123-125] For the exchange-correlation functional, we have used Perdew and Wang's gradient-corrected functionals.[126-128] Specifically, the line used in the Gaussian03 input deck is: # PW91PW91/Gen Pseudo=Read Opt SCF. The two basis sets, the all electron basis set 6-311++G** for carbon and oxygen and the pseudopotential basis set LANL2DZ for silver were read in explicitly in the input file. To test the effectiveness of these choices, we have used the Gaussian 03 suite of programs [129] to compute the ionization potentials (IP) and electron affinities (EA) of C, O, O₂, Ag and Ag₂ and also the optimized binding energies and bond lengths for CO, O₂, CO₂, and Ag₂⁻. The Berny optimization algorithm [130] has been used to find the global minimum energy structures. The SCF energy convergence is set to 10⁻⁸ Hartree, while the cutoff of maximum displacement for geometry optimization is set to 0.0018 Å, with the threshold of the maximum force being 0.00045 in atomic units. The results are listed in Table 1 and Table 2, respectively, and are compared with available

experimental data.[131] The results clearly indicate that these choices of the basis sets and exchange-correlation functionals produce reasonable results and they have been used for the rest of the computations.

Use of Ag_2^{-} for the catalytic oxidation of CO: (Scheme 1)

The calculated binding energies per atom and adsorption energies of different configurations are given in table 3. A positive binding energy implies stability and positive adsorption energy indicates the reaction is exothermic. The optimized structures of five different $Ag_2O_2^-$ complexes are shown in Figure 1(a – e). It can be seen that bonding of O₂ to Ag₂⁻ can take place in several ways with some configurations also showing Ag – Ag and O – O bond breaking. The end-bonded configuration shown in Figure 1a is the ground state (GS) configuration. The calculated binding energy per atom for this particular configuration is 2.13eV. As evident from the Figure 1a, oxygen is strongly bound to silver with an adsorption energy of 1.40eV which is in fairly good agreement with the experimental value of 1.12 eV.[24] This was also predicted for gold in which case the O_2 molecule was strongly and molecularly bound to Au₂.[103] Looking at the trend for these two metals, we can infer that O2 molecule has a tendency to bind rather strongly with transition metals. As can be seen from the figure, the two silver atoms together gets -0.41 of the total electronic charge, whereas the two oxygen atoms gets -0.58 of the total electronic charge. In this structure, more negative charge tends to stay with the two highly electronegative oxygen atoms. Figure 1b shows that oxygen can be side bonded to the silver anion dimer with a calculated binding energy per atom of 1.97eV, showing it to be less favorable than the GS structure. This

particular configuration has oxygen adsorption energy of 0.77eV. In this particular configuration the two silver atoms gets -0.66, whereas the two oxygen atoms together gets -0.33 of the total electronic charge. Here the Ag – O bond length is stretched by 0.75 Å compared to the GS structure making it less stable that the latter. Figure 1c shows oxygen bonded to Ag_2^- to form a deformed parallelogram with a binding energy per atom of 1.86eV. This configuration has the oxygen adsorption energy of 0.32eV. In this configuration, the two silver atoms gets most of the electronic charge, -0.77eV, compared to only -0.23eV that the two oxygen atoms get. Here the Ag_2^{-} bond length is stretched by 0.12 Å compared to the ground state structure and the Ag – O bond lengths are significantly stretched compared to the GS structure making it less stable. Figure 1d shows oxygen bonded to the silver anion dimer to form a rhombus with silver and oxygen atoms placed at alternate corners. This configuration has a binding energy per atom of 1.84eV with oxygen adsorption energy of 0.26eV. In this particular configuration all the negative charge goes to the two oxygen atoms, -1.24, whereas the two silver atoms have a 0.24 electronic charge. In this particular configuration, the Ag₂⁻ bond length is stretched by 0.05Å compared to the GS structure but the electronic charge goes to the oxygen atoms due to the O - O bond breaking. Figure 1e shows oxygen bonded to silver atoms in an alternate linear pattern with a binding energy per atom of 1.79eV. This configuration has an almost negligible oxygen adsorption energy of 0.005eV. Here the two oxygen atoms gets all the negative charge, -1.0, with the two silver atoms canceling a negative charge of -0.16 on one and 0.16 on the other. This particular structure is the least stable of all due to both, the Ag - Ag and O - O bond

breaking. This shows that when O_2 molecule is adsorbed without the O – O bond being broken, the configuration tends to be more stable. Considering the stabilities of the different configurations in which oxygen atoms bond to the silver anion dimer, the GS configuration in particular, suggests that oxygen adsorption to silver can be observed experimentally.

For Ag_2CO^2 , we found two different ways in which CO can attach itself to Ag_2^2 , as shown in figures 2(a - b), similar to Au₂CO⁻[103] For the end-bonded (GS) configuration, Figure 2a, the calculated adsorption energy of CO is 0.49eV and the binding energy per atom is 3.28eV, indicating that this system is highly stable and bound. In contrast, the calculated adsorption energy with gold is 0.96eV.[103] The distribution of electronic charges for individual atoms shows that most of the negative charge is shared by the two Ag atoms, while the CO together gets a charge of -0.28e. The electronic charge distribution shows that there is a overlapping between the wave functions of all the four atoms of Ag_2CO^{-} . In the second configuration, figure 2b, the binding energy per atom is 3.13eV, justifying it to be also a very stable cluster. But, in this particular configuration, the CO adsorption energy is -0.07eV, indicating that CO does not readily adsorb on Ag_2^- in this configuration. Particularly when the Ag - Agbond is broken or stretched to a high value of 3.94Å, the adsorption of CO to Ag₂⁻ is highly unlikely. This does indicate that CO can be attached to Ag₂ in different configurations, where the charges are mostly carried by the two silver atoms compared to the C and O atoms but the stability of the configuration depends on the whether Ag – Ag bond is broken or not. Figure 5 shows the optimized structure of Ag_2O^2 with a spin multiplicity of 2. Figure 6 shows the optimized structure of CO_2 with a spin multiplicity of 2. These structures are used in the discussions below for calculating the energies ΔE in the catalytic cycle.

We now move to the study of full catalytic cycle of oxidation of CO in presence of Ag₂⁻ : Ag₂⁻ + O₂ + CO + CO \rightarrow Ag₂⁻ + 2CO₂: Step (I) is the fundamental step of O₂ adsorption, which in our case was seen to occur without the O - O bond breaking as shown in Figure 1; Step (II) is the step in which CO adsorption to Ag₂⁻ occurs without the C – O bond breaking as shown in Figure 2. Here O_2 reacts with Ag_2^- before CO, as can be easily seen by the energy change of the two reactions ($\Delta E = 1.40 \text{eV}$ for step (I) and $\Delta E = 0.49 \text{eV}$ for step (II)). Hence step (II) is the reiteration of the fact that O₂ is more favorable to adsorb on Ag_2^- compared to CO. In accordance with the catalytic cycle, for step (III) a CO molecule in gas phase reacts with Ag₂O₂, leading to a number of different intermediate complexes, similar to the case for gold.[103] Among all these different intermediate complexes, the carbonate complex $Ag_2CO_3^-$, shown in Figure 3a, is most stable (GS). Describing the complex in a chain form $Ag - Ag - O^{(1)} - CO^{(2)} - CO^{(2$ $O^{(3)}$, the bond lengths are: d(Ag - Ag) = 2.61 Å; $d(Ag - O^{(1)}) = 2.23$ Å; $d(O^{(1)} - C) =$ 1.30 Å; and for the two C – $O^{(2),(3)}$ bonds d(C - O) = 1.27 Å. The O – CO₂ plane has an angle of 125.9° with the Ag – Ag – $O^{(1)}$ axis, the angle between $O^{(1)} – C – O^{(2),(3)}$ is 119.6° and the angle between $O^{(2)} - C - O^{(3)}$ is 120.6°. The corresponding numbers for Au, as obtained by Häkkinen and Landman [103], are 2.56 Å, 2.09 Å, 1.29 Å, 1.27 Å, 127.4°, 118.1°, and 123.8°. The binding energy per atom for this particular configuration is 4.03eV and the CO adsorption energy is 4.09eV. This structure is highly stable as the Ag_2^- dimer is end-bonded to the CO₃ (carbonate) molecule. Also, -0.91 of total electronic charge goes to the three O atoms while one of the Ag atoms gets only -0.19 of the total electronic charge. The other Ag and C atom together have a 0.10 of total electronic charge. This shows that, in the ground state, most of the electronic charge is shared by the three O atoms, as was found to be true for $Ag_2O_2^-$.

Three different stable configurations, figures 3b-3d, other than the most stable (GS) one shown in figure 3a, are possible for Ag₂CO₃⁻. In figure 3b, O₂⁻ and CO molecules are attached to the silver dimer in such a way that a chain of O – O – C – O is attached to the silver dimer via carbon. The binding energy per atom for this particular configuration is 3.44 eV and the CO adsorption energy is 0.56 eV which is very close to the configuration in Figure 3c, showing that they are almost equally stable. The interatomic distances are d (Ag – Ag) = 2.63 Å, d(Ag – C) = 2.16 Å, d(C – O⁽¹⁾) = 1.84 Å, d(O⁽¹⁾ – O⁽²⁾) = 1.31 Å, d(C – O⁽³⁾) = 1.17 Å and the angles are \angle (Ag – Ag – C) = 176° and \angle (C – O⁽¹⁾ – O⁽²⁾) = 112.4°. Figure 3c, is a co-adsorbed OC – Ag – Ag – O₂⁻, where a silver dimer is sandwiched between O₂⁻ and CO molecules. The binding energy per atom of this configuration is 3.41 eV and the CO adsorption energy is 0.41 eV. The inter-atomic distances for this configuration are d (Ag – Ag) = 2.63 Å, d(Ag – C) = 2.25 Å, d(Ag – O) = 2.29 Å, d(O – O) = 1.31 Å, d(C – O) = 1.16 Å and the angles are \angle (Ag – Ag – C) = 161.2° and \angle (Ag – O – O) = 116.5°.

In figure 3d, the CO molecule is adsorbed between the two Ag atoms and the O_2 molecule is end-bonded to one of the Ag atoms. Due to this the silver dimer is significantly stretched to 3.56 Å. The binding energy per atom of this particular

configuration is 3.33 eV and the CO adsorption energy is -0.06 eV. This shows that CO adsorption to $Ag_2O_2^-$ via breaking of the silver dimer is not feasible. The inter-atomic distances are $d(Ag^{(1)} - C) = 2.24$ Å, d(C - O) = 1.18 Å, $d(Ag^{(2)} - C) = 2.10$ Å, $d(Ag^{(2)} - O) = 2.16$ Å, d(O - O) = 1.33 Å and the angles are $\angle (Ag^{(1)} - C - Ag^{(2)}) = 110^\circ$ and $\angle (Ag^{(2)} - O - O) = 113.5^\circ$. All the above configurations have a spin multiplicity of 2. From the above discussions, we infer that the most stable configuration is the one in which the silver dimer is not broken and the three O atoms and one C atom tend to stay bonded rather than O₂ and CO molecule bonded on the two ends of silver dimer. The same conclusions have been drawn for Au₂⁻ by Häkkinen and Landman[103], and as pointed out by them, experimental results in this area would be very welcome.

The formation of this carbonate complex does not involve any activation barrier, and we predict the reaction (step III) to occur spontaneously. We determined the reaction barriers by constrained optimizations. In this process, we froze the reaction coordinate and all other geometrical parameters were optimized for the system to reach the minimum energy state. The reaction coordinate is the distance between the two atoms which was kept fixed, e.g., in our case, the distance between the C atom of the incoming CO molecule and one of the O atoms of the Ag₂O₂⁻ was kept fixed. The reaction coordinate was varied in increments of 0.05 - 0.1 Å to yield the respective total energies for each data point. This procedure provides a representation of the lowest energy path from the reactants to the products. We found that *no* reaction barrier exists and the reaction occurs spontaneously. This di-silver-carbonate is the most important intermediate compound in the reaction cycle, and with a high binding energy of 4.03eV

indicating the stability of the compound could be detected experimentally, as indicated before.

After the completion of step III, the reaction cycle can move forward in two different directions. Step (IVa) includes reaction of a CO molecule with Ag₂CO₃, which occurs spontaneously and does *not* require any activation barrier. A similar procedure as mentioned above was followed for calculating the reaction barrier for step IVa. In this case, the distance between one of the C atoms of the approaching CO molecule and one of the O atoms of the Ag₂CO₃⁻ was kept frozen and the geometry was then fully optimized. In this particular reaction, separation of two CO₂ molecules and the silver anion dimer can be observed distinctly. The end geometry for one of the optimized structures with the reaction coordinate as 3.1Å, where the two CO₂ molecules and one Ag₂ separates spontaneously is shown in Figure 4. This completes the cycle for producing two CO_2 molecules and Ag_2^- , and this, in turn, can be used for another cycle. In direct contrast, Häkkinen and Landman, [103] in their similar study for the reaction of a gas phase CO with $Au_2CO_3^-$, predicted an activation barrier of 0.5eV. Step (IVb) is endothermic and requires 1.97eV of energy to break the carbonate into a CO₂ molecule and a linear Ag_2O^{-} molecule. The corresponding value for the gold anion dimer[103] is 1.12eV. In the last step of the cycle (step V), Ag₂O⁻ reacts with another CO molecule to yield a Ag₂⁻ dimer and a CO₂ molecule. Although the catalytic cycle does not proceed after step (IVa), the last two steps, step (IVb) and step (V) gives an alternative path through which the reaction can proceed from step (IVa) and in turn yield a CO₂ molecule.

To verify the calculation of reaction barrier using constrained optimizations as described above, we also calculated the reaction barrier by investigating the possibility of transition states for reaction steps (III) and (IVa) using the Synchronous Transit-Guided Quasi-Newton (STQN) method[132-133] available in Gaussian 03.[129] In both reactions, presence of a maximum is not found and the final energy is found to be equal to the final optimized energy obtained before showing again that the reaction can proceed further without any supply of external energy and hence presence of any energy barrier is *not* seen. As an example, the optimized structure for step (III) found by the above STQN method is shown in figure 7. This structure is equivalent, energetically and geometrically, to the most stable optimized structure of $Ag_2CO_3^-$ shown in figure 3a. Hence, we can conclude that *no* reaction barrier is present in any of the reaction steps (III) and (IVa).

Use of Ag_2^+ *for the catalytic oxidation of CO*: (Scheme 2)

The calculated binding energies per atom and adsorption energies of different configurations involved in the catalytic cycle using Ag_2^+ as a catalyst are given in Table 3. A positive binding energy implies stability and positive adsorption energy indicates the reaction is exothermic. The optimized structures of five different $Ag_2O_2^+$ complexes are shown in Figure 1(a – e). It can be seen that bonding of O_2 to Ag_2^+ can take place in several ways with some configurations also showing Ag - Ag and O - O bond breaking. The end-bonded configuration shown in Figure 1a is the ground state (GS) configuration. The calculated binding energy per atom for this particular configuration is 2.02eV showing it to be highly stable. As evident from the Figure 1a,

oxygen is bound to silver with adsorption energy of 0.29eV. Comparing this to the most stable (GS) configuration of $Ag_2O_2^-$ with adsorption energy of 1.40eV, and a 2.13eV binding energy per atom [134], we conclude that O_2 gets more readily adsorbed on $Ag_2^$ compared to Ag_2^+ . As can be seen from the figure, the two silver atoms together gets 0.94 of the total electronic charge, while the two oxygen atoms gets -0.09 and 0.15 of the total electronic charge. Figure 1b shows that oxygen can be side bonded to the silver anion dimer with a calculated binding energy per atom of 2.01eV, showing it to be less favorable than the GS structure. This particular configuration has oxygen adsorption energy of 0.28eV. In this particular configuration the two silver atoms gets 1.44, whereas the two oxygen atoms gets -0.44 and 0.002 of the total electronic charge. Here the Ag – Ag bond is elongated to 4.30Å, showing that when the two Ag atoms are stretched too far, the configuration tends to be less stable.

Figure 1c shows oxygen bonded to Ag_2^+ to form a deformed parallelogram with a binding energy per atom of 1.99eV. This configuration has oxygen adsorption energy of 0.26eV. In this configuration, the two silver atoms gets most of the electronic charge, -0.91, compared to -0.06e and 0.15e of the two oxygen atoms. In this configuration the Ag – O bond is stretched significantly compared to the GS structure making it less stable. Figure 1d shows oxygen bonded to the silver cation dimer to form a rhombus with silver and oxygen atoms placed at alternate corners. This configuration has a binding energy per atom of 1.94eV with oxygen adsorption energy of -0.02eV. In this configuration the two Ag atoms gets 1.52 and the two O atoms gets -0.52 of the total electronic charge. This configuration involves breaking of the Ag – Ag bond making it less stable then the previous three structures. Figure 1e shows oxygen bonded to silver atoms in an alternate linear pattern with a binding energy per atom of 1.46eV. This configuration has an oxygen adsorption energy of -1.91eV. Here the two Ag atoms get 1.38 and the two O atoms get 0.10 and -0.50 of the total electronic charge. This particular structure is the least stable of all due to both, the Ag – Ag and O – O bond breaking. This shows that when O_2 molecule is adsorbed without the O – O and Ag – Ag bonds being broken, the configuration tends to be more stable. Considering the stabilities of the different configurations in which oxygen atoms bind to the silver cation dimer, the GS configuration, in particular, suggests that oxygen adsorption to silver can be observed experimentally.

For Ag_2CO^+ , we found two different ways in which CO can attach itself to Ag_2^+ , as shown in figures 2(a – b). For the end-bonded (GS) configuration, Figure 2a, the calculated adsorption energy of CO is 0.89eV and the binding energy per atom is 3.54eV, indicating that this system is highly stable and bound. Comparing this to the end-bonded (GS) configuration of Ag_2CO^- having binding energy per atom of 3.28eV and CO adsorption energy of 0.49eV, it can be said that CO gets more readily adsorbed on Ag_2^+ as compared to Ag_2^- .[134] In this configuration the two Ag atoms gets 0.74, whereas the C and O atom gets 0.36 and -0.10 of the total electronic charge, respectively. In the second configuration, figure 2b, the binding energy per atom is 3.43eV, justifying it also to be a very stable cluster. In this particular configuration, the CO adsorption energy is 0.46eV, indicating that CO does readily adsorb on Ag_2^+ in this configuration also. But due to the Ag – Ag bond being elongated to 3.79 Å, the configuration tends to be less stable compared to the GS configuration. Here the two Ag atoms get 1.04, whereas the C and the O atom get -0.11 and 0.07 of the total electronic charge, respectively. This does indicate that CO can be attached to Ag_2^+ in different configurations, where the charges are mostly carried by the two silver atoms compared to the C and O atoms but the comparative stability of the configuration depends on whether Ag – Ag bond is broken. Thus CO is more favorable to adsorb on Ag_2^+ compared to O₂. This is exactly opposite to the case of Ag_2^- , where O₂ was more favorable to adsorb on Ag_2^- , compared to CO.[134]

In accordance with the catalytic cycle, for step (III) a O₂ molecule in gas phase reacts with Ag₂CO⁺. The carbonate complex Ag₂CO₃⁺, shown in Figure 3a, is most stable (GS). Describing the complex in a chain form Ag – O⁽¹⁾ – Ag – O⁽²⁾ – C – O⁽³⁾ the bond lengths are: $d(Ag^{(1)} - O^{(1)}) = 2.38$ Å = $d(O^{(1)} - Ag^{(2)})$, $d(Ag^{(1)} - O^{(2)}) = 2.29$ Å = $d(O^{(3)} - Ag^{(2)})$, $d(C - O^{(1)}) = 1.31$ Å and for the two C – O^{(2),(3)} bonds d(C - O) = 1.27Å. The angles between the atoms are: $\angle Ag^{(1)} - O^{(1)} - Ag^{(2)} = 180^{\circ}$, $\angle O^{(1)} - C - O^{(2)} =$ 120° , $\angle C - O^{(2)} - Ag^{(1)} = 95.36^{\circ}$. The binding energy per atom for this particular configuration is 3.94eV and the O₂ adsorption energy is 3.45eV. This configuration is highly stable as the CO₃ (carbonate) molecule tends to stay together, the fact that was also seen in the Ag₂CO₃⁻ configuration. Here the three O atoms gets a total of -0.89 of the total electronic charge, whereas the C atom gets 0.48 and the two Ag atoms gets 1.42 of the total electronic charge. This shows that for the GS configuration the two Ag atoms gets most of the positive charge, which was not the case for the GS configuration of Ag₂CO₃⁻, where the three O atoms got most of the negative charge.[134]

Three different stable configurations, figures 3b-3d, other than the most stable (GS) one shown in figure 3a, are also possible for $Ag_2CO_3^+$. In figure 3b, the O_2 molecule is adsorbed between the two Ag atoms and the CO molecule is end-bonded to one of the Ag atoms. Due to this the silver dimer is significantly stretched to 4.16 Å. The binding energy per atom of this particular configuration is 3.47 eV and the O_2 adsorption energy is 0.58 eV. This shows that even though the Ag – Ag bond is broken, the adsorption of O_2 molecule is possible which was not true for the case of $Ag_2CO_3^-$, where a similar configuration was least stable with a negative adsorption energy of -0.06eV.[134] In this particular configuration the two Ag atoms get 1.18 of the total electronic charge, the C atom gets 0.33 and the three O atoms together gets -0.51 of the total electronic charge. The inter-atomic distances are $d(Ag^{(1)} - O^{(1)}) = 2.24$ Å, $d(O^{(1)} - O^{(1)}) = 2.24$ Å, $d(O^{(1$ $O^{(2)}$) = 1.29 Å, $d(O^{(2)} - Ag^{(2)}) = 2.15$ Å, $d(Ag^{(2)} - C) = 2.07$ Å, and $d(C - O^{(3)}) = 1.13$ Å. The angles between the individual atoms are: $\angle (Ag^{(1)} - O^{(1)} - O^{(2)}) = 132.8^{\circ}$, $\angle (O^{(1)} - O^{(2)} - Ag^{(2)}) = 137.1^{\circ}, \ \angle (O^{(2)} - Ag^{(2)} - C) = 173.9^{\circ}, \text{ and } \angle (Ag^{(2)} - C - O^{(3)})$ $= 179.8^{\circ}.$

Figure 3c, is a co-adsorbed OC – Ag – Ag – O₂, where a silver dimer is sandwiched between O₂ and CO molecules. The binding energy per atom of this configuration is 3.41eV and the O₂ adsorption energy is 0.24eV. Here even though the Ag – Ag bond is not broken, the configuration is less stable due to the fact that the CO₃ molecule does not stay bonded. In this particular configuration the two Ag atoms get 0.68 of the total electronic charge, whereas the three O atoms together get -0.03 and the C atom gets 0.35 of the total electronic charge. The inter-atomic distances are $d(O^{(1)} -$ C) = 1.13 Å, $d(C - Ag^{(1)}) = 2.18$ Å, $d(Ag^{(1)} - Ag^{(2)}) = 2.76$ Å, $d(Ag^{(2)} - O^{(2)}) = 2.47$ Å, and $d(O^{(2)} - O^{(3)}) = 1.22$ Å. The angles between the individual atoms are: $\angle (O^{(1)} - C - Ag^{(1)}) = 179^{\circ}$, $\angle (C - Ag^{(1)} - Ag^{(2)}) = 178.1^{\circ}$, $\angle (Ag^{(1)} - Ag^{(2)} - O^{(2)}) = 174.1^{\circ}$, and $\angle (Ag^{(2)} - O^{(2)} - O^{(3)}) = 129.8^{\circ}$.

In Figure 3d, the CO₃ molecule is end-bonded to the Ag dimer via C atom. This structure is the least stable of all with a binding energy per atom of 2.92eV and O_2 adsorption energy of -2.61eV, showing that O2 adsorption is not feasible in this particular configuration. In this configuration even though the Ag - Ag bond is not broken and the CO₃ molecule stays bonded the structure is least stable as the CO₃ molecule does not have a tetrahedral symmetry. Here the two Ag atoms get 0.74 of the total electronic charge, whereas the three O atoms together get 0.28 and the C atom gets -0.04 of the total electronic charge. The inter-atomic distances are $d(Ag^{(1)} - Ag^{(2)}) =$ 2.77 Å, $d(Ag^{(2)} - C) = 2.16$ Å, $d(C - O^{(1)}) = 1.31$ Å, $d(O^{(1)} - O^{(2)}) = 1.51$ Å, and $d(O^{(2)}) = 1.51$ Å, and d $-O^{(3)} = 1.51$ Å, and $d(O^{(3)} - C) = 1.31$ Å. The angles between the individual atoms are: $\angle (Ag^{(1)} - Ag^{(2)} - C) = 179.8^{\circ}, \ \angle (Ag^{(2)} - C - O^{(1)}) = 130.45^{\circ}, \ \angle (C - O^{(1)} - O^{(2)})$ 89.33°, $\angle (O^{(1)} - O^{(2)} - O^{(3)}) = 99.1^{\circ}$, and $\angle (O^{(2)} - O^{(3)} - C) = 89.33^{\circ}$. From the above discussions, we infer that the most stable configuration is the one in which the three O atoms and one C atom tend to stay bonded and have a tetrahedral symmetry rather than O₂ and CO molecule bonded on the two ends of silver dimer. In this case even though the silver dimer is broken (Figure 3a) which was not true for the case of $Ag_2CO_3^-$, the configuration tends to be highly stable due to the fact that tetrahedral symmetry is preserved.
We calculated the reaction barrier by investigating the possibility of transition states for reaction steps (III) and (IVa) using the Synchronous Transit-Guided Quasi-Newton (STQN) method[132-133] available in Gaussian 03.[129] In both reactions, presence of a maximum was found and the final energy of the transition state structure was found to be higher than the final optimized energy obtained before showing that the reaction can proceed further only if external energy is supplied. Hence presence of a reaction barrier for both the reactions is predicted. As an example, for the reaction involving the formation of the carbonate complex, step (III), the optimized structure found by the above STQN method is shown in figure 4. This structure was found to be energetically higher and geometrically different to the most stable optimized structure of Ag₂CO₃⁺ shown in figure 3a. Here the reaction barrier for step (III) was found to be 0.68eV. Similarly the reaction barrier for reaction step (IVa) was found to be 1.21eV. The same reactions did *not* show any reaction barrier in the case of silver anion dimer being used as a catalyst.[134] In the last step of the cycle (step V), Ag₂O⁺ reacts with another CO molecule to yield a Ag_2^+ dimer and a CO_2 molecule. Although the catalytic cycle does not proceed after step (IVa), the last two steps, step (IVb) and step (V) gives an alternative path through which the reaction can proceed from step (IVa) and in turn yield a CO₂ molecule.

Use of Ag₂ for the catalytic oxidation of CO: (Scheme 3)

Proceeding now to understand the charge state effects, we next studied the catalytic cycle using Ag_2 as a catalyst. The calculated binding energies per atom and adsorption energies of different configurations involved in the catalytic cycle using Ag_2 as a catalyst are given in Table 4. The optimized structures of four different Ag_2O_2 complexes are shown in Figure 5(a – d). It can be seen that similar to the case of Ag_2^{-1} and Ag_2^+ , bonding of O_2 to Ag_2 can take place in several ways with some configurations also showing Ag – Ag and O – O bond breaking. The end-bonded configuration shown in Figure 5a is the ground state (GS) configuration. The calculated binding energy per atom for this particular configuration is 2.02eV showing it to be highly stable. As evident from the Figure 5a, oxygen is bound to silver with a adsorption energy of 0.23eV. Comparing this to the most stable (GS) configuration of $Ag_2O_2^-$ having adsorption energy of 1.40eV, a binding energy per atom of 2.13eV,[43] and to the most stable (GS) configuration of $Ag_2O_2^+$ having a adsorption energy of 0.29eV, a binding energy per atom of 2.02eV, it can be said that O₂ gets more readily adsorbed on Ag₂⁻ compared to Ag_2^+ and Ag_2 . As can be seen from the figure, the two silver atoms together gets 0.12 of the total electronic charge, while the two oxygen atoms gets -0.14 and 0.02 of the total electronic charge. Also the Ag - Ag bond length is compressed to 2.60 Å for the neutral case, from 2.76 Å for the cationic and 2.64 Å for the anionic case. Figure 5b shows that oxygen can be side bonded to the silver neutral dimer with a calculated binding energy per atom of 1.96eV, showing it to be less favorable than the GS structure. This particular configuration has oxygen adsorption energy of 0.19eV. In this particular configuration the two silver atoms gets 0.46, whereas the two oxygen atoms gets -0.46 of the total electronic charge. Here the Ag - O bond is elongated to 2.99Å, showing that when the oxygen dimer is side-bonded far from the silver dimer the configuration tends to be less stable then the GS configuration.

Figure 5c shows oxygen bonded to silver atoms in an alternate linear pattern with a binding energy per atom of 1.65eV. This configuration has oxygen adsorption energy of -1.24eV showing that oxygen adsorption in this configuration is not feasible. Here the two Ag atoms get 0.90 and the two O atoms get -0.90 of the total electronic charge. This particular structure is the less stable due to the fact that it involves both, Ag - Ag and O - O bond breaking. Figure 5d shows oxygen bonded to the silver anion dimer to form a rhombus with silver and oxygen atoms placed at alternate corners. This configuration has a binding energy per atom of 1.63eV with oxygen adsorption energy of -1.27eV. In this configuration the two Ag atoms gets 0.86 and the two O atoms gets -0.86 of the total electronic charge. This configuration involves the breaking of O - Obond and also the Ag – Ag bond is stretched too far making it the least stable of all the configurations. This shows that when O_2 molecule is adsorbed without the O - O and Ag – Ag bond being broken, the configuration tends to be more stable. Considering the stabilities of the different configurations in which oxygen atoms bind to the silver neutral dimer, the GS configuration in particular, suggests that oxygen adsorption to silver can be observed experimentally. Also comparing all the results from $Ag_2O_2^{-,2}$ $Ag_2O_2^+$, and Ag_2O_2 it can be said that regardless of the charge state, the $Ag_2O_2^*$ configuration (* = -, +, or 0) in which the oxygen dimer is end-bonded to the silver dimer, without the Ag - Ag or the O - O bond being broken, proves to be the most stable.

For Ag_2CO , we found two different ways in which CO can attach itself to Ag_2 , as shown in figures 6(a – b). For the end-bonded (GS) configuration, Figure 6a, the calculated adsorption energy of CO is 0.45eV and the binding energy per atom is 3.45eV, indicating that this system is highly stable and bound. Comparing this to the end-bonded (GS) configuration of Ag_2CO^+ having binding energy per atom of 3.54eV and CO adsorption energy of 0.89eV, and to the end-bonded (GS) configuration of Ag₂CO⁻ having binding energy per atom of 3.28eV and CO adsorption energy of 0.49eV,[134] it can be said that CO gets more readily adsorbed on Ag_2^+ and Ag_2^- then on Ag₂. In this configuration the two Ag atoms get -0.08 and 0.02 of the total electronic charge, whereas the C and O atom gets 0.14 and -0.08 of the total electronic charge, respectively. In the second configuration, figure 6b, the binding energy per atom is 3.18eV, justifying it to be a very stable cluster. In this particular configuration, the CO adsorption energy is -0.56eV, indicating that CO adsorption on Ag₂ in this particular configuration is not feasible. Here due to the Ag – Ag bond being elongated to 3.78 Å, the configuration tends to be less stable compared to the GS configuration. Here the two Ag atoms get 0.26, whereas the C and the O atom get -0.25 and -0.01 of the total electronic charge, respectively. This does indicate that CO can be attached to Ag₂ in different configurations, but the stability of the configuration depends on the whether Ag – Ag bond is broken or not. Again comparing all the results from Ag₂CO⁻,[134] Ag_2CO^+ , and Ag_2CO it can be said that regardless of the charge state, the Ag_2CO^* configuration (* = -, +, or 0) in which the carbon monoxide molecule is end-bonded to the silver dimer, without the Ag – Ag or the C – O bond being broken, proves to be the most stable. Again, CO reacts with Ag₂ before O₂, as can be easily seen by the energy

change of the two reactions ($\Delta E = 0.23 \text{eV}$ for step (I) and $\Delta E = 0.45 \text{eV}$ for step (II)). This is exactly opposite to the case of Ag₂⁻, but is similar to the case of Ag₂⁺.

In accordance with the catalytic cycle, for step (III) a O_2 molecule in gas phase reacts with Ag₂CO, leading to a number of different intermediate complexes, similar to the case for Ag_2^+ and Ag_2^- .[134] Among all these different intermediate complexes, the carbonate complex Ag₂CO₃, shown in Figure 7a, is most stable (GS). Describing the complex in a chain form $Ag^{(1)} - Ag^{(2)} - O^{(1)} - O^{(3)} - CO^{(2)}$, the bond lengths are: $d(Ag^{(1)} - Ag^{(2)}) = 2.67 \text{ Å}, d(Ag^{(2)} - O^{(1)}) = 2.17 \text{ Å}, d(Ag^{(2)} - O^{(3)}) = 2.31 \text{ Å}, d(O^{(1)} - C) = 2.31$ 1.33 Å, $d(O^{(2)} - C) = 1.24$ Å and $d(O^{(3)} - C) = 1.28$ Å. The angles between the atoms are: $\angle Ag^{(1)} - Ag^{(2)} - O^{(1)} = 98.77^{\circ}, \ \angle O^{(1)} - Ag^{(2)} - O^{(3)} = 59.53^{\circ}, \ \angle O^{(1)} - C - O^{(2)} = 59.53^{\circ}$ 115.26°, $\angle O^{(2)} - C - O^{(3)} = 127.48^{\circ}$, $\angle O^{(1)} - C - O^{(3)} = 117.24^{\circ}$. The binding energy per atom for this particular configuration is 3.72eV and the O₂ adsorption energy is 2.55eV. This configuration is highly stable as the CO_3 (carbonate) molecule tends to stay together having a tetrahedral symmetry and is end-bonded to the silver neutral dimer, the fact that was also seen in the $Ag_2CO_3^+$ and $Ag_2CO_3^-$ configuration.[134] Here the three O atoms gets a total of -0.80 of the total electronic charge, whereas the C atom gets 0.32 and the two Ag atoms gets 0.48 of the total electronic charge.

Three different stable configurations, figures 7b-7d, other than the most stable (GS) one shown in figure 7a, are possible for Ag_2CO_3 . Figure 7b, is a co-adsorbed OC – $Ag - Ag - O_2$, where a silver dimer is sandwiched between O_2 and CO molecules. The binding energy per atom of this configuration is 3.34eV and the O_2 adsorption energy is 0.19eV. Here even though the Ag - Ag bond is not broken, the configuration is less

stable due to the fact that the CO₃ molecule does not stay bonded. In this particular configuration the two Ag atoms get 0.05 and -0.03 of the total electronic charge, whereas the three O atoms together get -0.09, -0.09 and 0.01 of the total electronic charge and the C atom gets 0.15 of the total electronic charge. The inter-atomic distances are $d(O^{(1)} - C) = 1.14$ Å, $d(C - Ag^{(1)}) = 2.18$ Å, $d(Ag^{(1)} - Ag^{(2)}) = 2.61$ Å, $d(Ag^{(2)} - O^{(2)}) = 2.43$ Å, and $d(O^{(2)} - O^{(3)}) = 1.24$ Å. The angles between the individual atoms are: $\angle (O^{(1)} - C - Ag^{(1)}) = 145.22^{\circ}$, $\angle (C - Ag^{(1)} - Ag^{(2)}) = 159.57^{\circ}$, $\angle (Ag^{(1)} - Ag^{(2)}) = 170.13^{\circ}$, and $\angle (Ag^{(2)} - O^{(2)} - O^{(3)}) = 121.51^{\circ}$.

In Figure 7c, the CO₃ molecule is end-bonded to the Ag dimer via C atom. This configuration has a binding energy per atom of 3.29eV and O₂ adsorption energy of 0.03eV, showing that O₂ adsorption is feasible but unlikely in this particular configuration. In this configuration even though the Ag – Ag bond is not broken and the CO₃ molecule stays bonded the structure is less stable as the CO₃ molecule does not have a tetrahedral symmetry and also the O⁽¹⁾ – O⁽²⁾ bond length is significantly stretched to 2.98 Å. In this particular configuration the two Ag atoms get -0.09 and 0.05 of the total electronic charge, whereas the three O atoms get -0.02, -0.09, 0.09 and the C atom gets -0.09 of the total electronic charge. The inter-atomic distances are $d(Ag^{(1)} - Ag^{(2)}) = 2.59$ Å, $d(Ag^{(2)} - C) = 2.17$ Å, $d(C - O^{(1)}) = 1.14$ Å, $d(O^{(1)} - O^{(2)}) = 2.98$ Å, and $d(O^{(2)} - O^{(3)}) = 1.22$ Å. The angles between the individual atoms are: $\angle (Ag^{(1)} - Ag^{(2)} - C) = 160.5^{\circ}$, $\angle (Ag^{(2)} - C - O^{(1)}) = 144.48^{\circ}$, $\angle (C - O^{(1)} - O^{(2)}) = 180^{\circ}$ and, $\angle (O^{(1)} - O^{(2)} - O^{(3)}) = 175.2^{\circ}$.

In figure 7d, the CO molecule is adsorbed between the two Ag atoms via C atom and the O₂ molecule is end-bonded to one of the Ag atoms. Due to this the silver dimer is significantly stretched to 3.59 Å. This configuration is the least stable with a binding energy per atom of 3.22eV and the O₂ adsorption energy is -0.57eV. This shows that as the Ag – Ag bond is stretched too far and the CO3 molecule is broken, the adsorption of O₂ molecule is not feasible for this particular configuration which was also true for the case of Ag₂CO₃, where a similar configuration was least stable with negative adsorption energy of -0.06eV. In this particular configuration the two Ag atoms get 0.49 of the total electronic charge, the C atom gets -0.19 and the three O atoms together gets -0.30 of the total electronic charge. The inter-atomic distances are $d(O^{(1)} - O^{(2)}) = 1.27$ Å, $d(O^{(2)} - Ag^{(1)}) = 2.24$ Å, $d(Ag^{(1)} - C) = 2.12$ Å, $d(C - O^{(3)}) = 1.17$ Å, and $d(C - C^{(3)}) = 0.17$ Å Å, and $d(C - C^{(3)}) = 0.17$ Å $Ag^{(2)}$) = 2.19 Å. The angles between the individual atoms are: $\angle (O^{(1)} - O^{(2)} - Ag^{(1)}) =$ 115.9°, $\angle (O^{(2)} - Ag^{(1)} - C) = 178.8^{\circ}$, $\angle (Ag^{(1)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$, and $\angle (O^{(3)} - C - Ag^{(2)}) = 112.9^{\circ}$. $Ag^{(2)}$) = 118.8°. From the above discussions, we infer that the most stable configuration for the carbonate complex is the one in which the three O atoms and one C atom tend to stay bonded and have a tetrahedral symmetry rather than O_2 and CO molecule bonded on the two ends of silver dimer. Also comparing the most stable configurations for all the three cases, $Ag_2CO_3^{-25}Ag_2CO_3^{+}$ and Ag_2CO_3 , the common feature which prevails is that the CO₃ (carbonate) molecule tends to stay together with a tetrahedral symmetry.

Similar to the calculation of reaction barrier for the reactions from the catalytic cycle using Ag_2^+ as a catalyst, we calculated the reaction barrier for the reactions from the catalytic cycle using Ag_2 as a catalyst. In both reactions again, presence of a maximum

was found and the final energy of the transition state structure was found to be higher than the final optimized energy obtained before showing that the reaction can proceed further only if external energy is supplied. Hence presence of a reaction barrier for both the reactions is predicted. As an example, for the reaction involving the formation of the carbonate complex, step (III), the optimized structure found by the above STQN[132-133] method is shown in figure 8. This structure was found to be energetically higher and geometrically different to the most stable optimized structure of Ag_2CO_3 shown in figure 7a. Here the reaction barrier for step (III) was found to be 0.08eV. Even though in this case the reaction barrier is rather negligible, there is a definite reaction barrier and it can be said that the reaction will not proceed further without supply of energy. Similarly the reaction barrier for reaction step (IVa) was found to be 0.92eV. In the last step of the cycle step (V), Ag₂O reacts with another CO molecule to yield Ag₂ dimer and a CO₂ molecule. Although the catalytic cycle does not proceed after step (IVa), the last two steps, step (IVb) and step (V) gives an alternative path through which the reaction can proceed from step (IVa) and in turn yield a CO₂ molecule.

Conclusion:

To conclude, gas phase catalytic oxidation of CO can be achieved using Ag_2^- as the catalyst. Also silver proves to be a better catalyst than gold since for gold, steps (III) and (IVa) require activation barrier of 0.3 eV and 0.5 eV respectively.[103] It appears that oxidation of CO can be achieved, cost effectively, at room temperature using silver, without any supply of external energy. Also gas phase catalytic oxidation of CO can be achieved using Ag_2^+ and Ag_2 as catalysts. Our comparative study of the catalytic

cycles for Ag_2^- ,[134] Ag_2^+ , and Ag_2 , indicates that Ag_2^- performs better as a catalyst compared to Ag_2^+ and Ag_2 . This can be seen from the fact that the reaction steps (III) and (IVa) for Ag_2^+ and Ag_2 show presence of reaction barriers, not observed for the same reactions involving Ag_2^- as a catalyst.





Figure A.1 Possible configurations of $Ag_2O_2^-$: Different stable configurations (a), (b), (c) and (d).



Figure A.1 Possible configurations of $Ag_2O_2^-$: Different stable configurations (e).



(a) (b) Figure A.2 Possible configurations of Ag_2CO^2 : Different stable configurations (a) and (b).





Figure A.3 Possible configurations of $Ag_2CO_3^-$: Different stable configurations (a), (b), (c) and (d).



Figure A.4 One of the structure in the reaction step IVa in the catalytic cycle. Here for finding the reaction barrier one of the bond length between two O atoms is kept as 3.1 Å. Here the two CO₂ molecules detach easily from Ag₂⁻ dimer showing the reaction to be occurring spontaneously without any supply of external energy.





Figure A.7 Final structure for reaction step (III) by the STQN method.



Figure A.8 Possible configurations of $Ag_2O_2^+$: Different stable configurations (a), (b), (c) and (d).



Figure A.8 Possible configurations of $Ag_2O_2^+$: Different stable configurations (e).



Figure A.9 Possible configurations of Ag_2CO^+ : Different stable configurations (a) and (b).



(b), (c) and (d).



Figure A.11 Final structure for reaction step (III) by the STQN method.



Figure A.12 Possible configurations of Ag_2O_2 : Different stable configurations (a), (b), (c) and (d).



Figure A.13 Possible configurations of Ag_2CO : Different stable configurations (a) and (b).



(c) (d) Figure A.14 Possible configurations of Ag₂CO₃: Different stable configurations (a), (b), (c) and (d).



Figure A.15 Final structure for reaction step (iii) by the STQN method.

Scheme 1. A Catalytic cycle yielding 2 CO2 molecules using Ag2 as a catalyst*

$$Ag_2^- + O_2 \rightarrow Ag_2O_2^- \qquad \Delta E = -1.40$$
 (I)

$$Ag_2^- + CO \rightarrow Ag_2CO^- \qquad \Delta E = -0.49$$
 (II)

$$Ag_2O_2^- + CO \rightarrow Ag_2CO_3^- \qquad \Delta E = -4.10$$
 (III)

$$Ag_2CO_3^- + CO \rightarrow Ag_2^- + 2CO_2 \qquad \Delta E = -1.11$$
 (IVa)

$$Ag_2CO_3 \rightarrow Ag_2O + CO_2 \qquad \Delta E = +1.97 \qquad (IVb)$$

$$Ag_2O^- + CO \rightarrow Ag_2^- + CO_2 \qquad \Delta E = -3.08 \qquad (V)$$

* Each step shows the calculated energy change, ΔE , with respect to the previous step. (ΔE was calculated using the formula: $\Delta E = E_n [RHS] - E_n [LHS]$, where $E_n [RHS]$ is the sum of the total energies of different molecules on the Right Hand Side and $E_n [LHS]$ is the sum of the total energies of different molecules on the Left Hand Side of the above equation steps). The initial reference energy is the sum of the gas-phase energies $E(Ag_2^-) + E(O_2) + 2E(CO)$. All the above energies are given in eV. A negative energy value corresponds to an exothermic step, whereas a positive energy value corresponds to an endothermic step. Scheme 2. A Catalytic cycle yielding 2 CO_2 molecules using Ag_2^+ as a catalyst

$$Ag_2^+ + O_2 \rightarrow Ag_2O_2^+ \qquad \Delta E = -0.29 \text{ eV}$$
 (I)

$$Ag_2^+ + CO \rightarrow Ag_2CO^+ \qquad \Delta E = -0.89 \text{ eV}$$
 (II)

$$Ag_2CO^+ + O_2 \rightarrow Ag_2CO_3^+ \qquad \Delta E = -3.45 \text{ eV}$$
 (III)

$$Ag_2CO_3^+ + CO \rightarrow Ag_2^+ + 2CO_2 \qquad \Delta E = -2.28 \text{ eV}$$
 (IVa)

$$Ag_2CO_3^+ \rightarrow Ag_2O^+ + CO_2 \qquad \Delta E = +1.67 \text{ eV}$$
 (IVb)

$$Ag_2O^+ + CO \rightarrow Ag_2^+ + CO_2 \qquad \Delta E = -3.93 \text{ eV} \quad (V)$$

Scheme 3. A Catalytic cycle yielding 2 CO_2 molecules using Ag₂ as a catalyst

$Ag_2 + O_2 \rightarrow Ag_2O_2$	$\Delta E = -0.23 \text{ eV}$	(I)
$Ag_2 + CO \rightarrow Ag_2CO$	$\Delta E = -0.45 \text{ eV}$	(II)
$Ag_2CO + O_2 \rightarrow Ag_2CO_3$	$\Delta E = -2.55 \text{ eV}$	(III)
$Ag_2CO_3 + CO \rightarrow Ag_2 + 2CO_2$	$\Delta E = -1.84 \text{ eV}$	(IVa)
$Ag_2CO_3 \rightarrow Ag_2O + CO_2$	$\Delta E = +1.23 \text{ eV}$	(IVb)
$Ag_2O + CO \rightarrow Ag_2 + CO_2$	$\Delta E = -4.85 \text{ eV}$	(V)

Element	Theory		Exp ³²	
	EA	IP	EA	IP
0	1.731	14.12	1.461	13.61
С	0.951	11.59	1.262	11.26
O ₂	0.519	12.39	0.451	12.07
Ag	1.109	7.84	1.302	7.57
Ag ₂	1.011	7.89	1.023	7.61

Table A.1. Ionization potentials and electron affinities (in eV) of O, C, O₂, Ag, and Ag₂.

Table A.2. Binding energies E_b (in eV) and bond lengths d (in Å) of CO, O₂, CO₂, and Ag₂.

Element	Theory		Exp ³²	
	E _b	D	E _b	d
СО	11.54	1.136	11.16	1.128
O ₂	6.06	1.209	5.18	1.207
CO2	11.92	1.17	11.02	1.16
Ag ₂	1.78	2.59	1.66 ^(a)	2.48 ^(a)
Ag ₂	1.68	2.73	1.39	2.84

^(a) These	experimental	values are	quoted in	1 reference	34
THUSU	слрегинстна	values are	quoted II		J - .

Figure	Configuration	Μ	E _b /n	Ea
1a	Ag ₂ O ₂ ⁻	2	2.13	1.4
1b	Ag ₂ O ₂	2	1.97	0.77
1c	Ag ₂ O ₂	4	1.86	0.32
1d	Ag ₂ O ₂	2	1.84	0.26
1e	$Ag_2O_2^-$	4	1.79	0.005
2a	Ag ₂ CO ⁻	2	3.28	0.49
2b	Ag ₂ CO ⁻	2	3.13	-0.07
3а	Ag ₂ CO ₃ ⁻	2	4.03	4.09
3b	Ag ₂ CO ₃ ⁻	2	3.44	0.56
Зс	Ag ₂ CO ₃ ⁻	2	3.41	0.41
3d	Ag ₂ CO ₃ ⁻	2	3.33	-0.06

Table A.3. Binding energies per atom and adsorption energies (all in eV) of CO with Ag_2^- , O_2 with Ag_2^- , and CO with $Ag_2O_2^-$.

Figure	Configuration	М	E _b /n	Ea
1a	$Ag_2O_2^+$	2	2.02	0.29
1b	$Ag_2O_2^+$	2	2.01	0.28
1c	$Ag_2O_2^+$	2	1.99	0.26
1d	$Ag_2O_2^+$	2	1.94	-0.02
1e	$Ag_2O_2^+$	2	1.46	-1.91
2a	Ag_2CO^+	2	3.54	0.89
2b	Ag_2CO^+	2	3.43	0.46
3а	$Ag_2CO_3^+$	2	3.94	3.45
3b	$Ag_2CO_3^+$	2	3.47	0.58
Зс	$Ag_2CO_3^+$	2	3.41	0.24
3d	$Ag_2CO_3^+$	2	2.92	-2.61

Table A.4. Binding energies per atom and adsorption energies (all in eV) of CO with Ag_2^+ , O_2 with Ag_2^+ , and O_2 with Ag_2CO^+ , and respective spin multiplicities M for each of the configuration.

Figure	Configuration	Μ	E _b /n	Ea
5a	Ag ₂ O ₂	3	2.02	0.23
5b	Ag ₂ O ₂	1	1.96	0.19
5c	Ag ₂ O ₂	3	1.65	-1.24
5d	Ag ₂ O ₂	3	1.63	-1.27
6a	Ag ₂ CO	1	3.45	0.45
6b	Ag ₂ CO	1	3.18	-0.56
7a	Ag ₂ CO ₃	1	3.72	2.55
7b	Ag ₂ CO ₃	3	3.34	0.19
7c	Ag ₂ CO ₃	3	3.29	0.03
7d	Ag ₂ CO ₃	3	3.22	-0.57

Table A.5. Binding energies per atom and adsorption energies (all in eV) of CO with Ag_2 , O_2 with Ag_2 , and O_2 with Ag_2CO , and respective spin multiplicities M for each of the configuration.

-6.9964	47.8754	86.9762
111.9512	133.1244	169.259
529.1899	573.5933	700.113
1000.3272	1166.7272	1251.3615

Table A.6. Vibration frequencies in cm⁻¹ for the transition state structure III for Ag_2^+ :

Table A.7. Vibration frequencies in cm^{-1} for the transition state structure III for Ag₂:

43.0455	71.3979	147.2817
149.1494	222.9423	273.8197
508.5719	605.9595	765.1271
977.6714	1281.0212	1552.1853

APPENDIX B

INPUT COORDINATES FOR BARE URANIUM AND OXYGEN, CARBON AND CARBON MONOXIDE ADSORBED URANIUM SURFACES

Table B.1. Coordinates for bare uranium

U1	0.000000000	0.000000000	0.000000000
U2	0.000000000	3.467000000	0.000000000
U3	3.467000000	0.000000000	0.000000000
U4	3.467000000	3.467000000	0.000000000
U5	0.000000000	0.000000000	3.467000000
U6	0.000000000	3.467000000	3.467000000
U7	3.467000000	0.000000000	3.467000000
U8	3.467000000	3.467000000	3.467000000
U9	1.733500000	1.733500000	1.733500000
U10	1.733500000	5.200500000	1.733500000
U11	5.200500000	1.733500000	1.733500000
U12	5.200500000	5.200500000	1.733500000

Table B.2. Coordinates for oxygen adatom adsorbed on uranium surface at the top site

O 3.435714000 3.434112246 -1.680221444

Table B.3. Coordinates for oxygen adatom adsorbed on uranium surface at the bridge site

O 3.460692626 5.209633326 -1.062332606

Table B.4. Coordinates for oxygen adatom adsorbed on uranium surface at the center site

O 1.743740409 5.200500000 -0.531109577

Table B.5. Coordinates for oxygen adatom adsorbed on uranium surface at the interstitial site

O 3.466690882 3.458088285 1.732182309

Table B.6. Coordinates for carbon adatom adsorbed on uranium surface at the top site

C 3.426396160 3.463670293 -1.777245289

Table B.7. Coordinates for carbon adatom adsorbed on uranium surface at the bridge site

C 3.395920606 5.192421127 -1.131664517

Table B.8. Coordinates for carbon adsorbed uranium for the center site

C 1.717603944 5.200500000 -0.813781899

Table B.9. Coordinates for carbon adsorbed uranium for the interstitial site

C 3.480146587 3.559924129 1.762301939

Table B.10. Coordinates for CO molecule adsorbed on uranium surface at the top site with Vert1 approach

O 3.513847976 3.506712682 -3.187134699

C 3.529815938 3.588413300 -4.326032104

Table B.11. Coordinates for CO molecule adsorbed on uranium surface at the top site with Vert2 approach

C 3.509548203 3.507282726 -2.713948802

O 3.513847976 3.506712682 -3.855805359

Table B.12. Coordinates for CO molecule adsorbed on uranium surface at the top site with Hor1 approach

O 4.102017870 3.455339786 -2.843061476

C 2.962268593 3.383693190 -2.872269800

Table B.13. Coordinates for CO molecule adsorbed on uranium surface at the top site with Hor2 approach

O 3.853045874 3.822438573 -2.738233796

C 3.093110746 2.978800844 -2.743958326

Table B.14. Coordinates for CO molecule adsorbed on uranium surface at the bridge site with Vert1 approach

O 3.432863918 5.040407808 -2.792486480

C 3.429181964 5.070612312 -3.933878515

Table B.15. Coordinates for CO molecule adsorbed on uranium surface at the bridge site with Vert2 approach

- C 3.432866276 5.040406976 -1.587842484
- O 3.429181548 5.070608914 -2.729069527

Table B.16. Coordinates for CO molecule adsorbed on uranium surface at the bridge site with Hor1 approach

O 3.483880476 5.802354350 -2.395062174

C 3.479479050 4.661561576 -2.381353756

Table B.17. Coordinates for CO molecule adsorbed on uranium surface at the bridge site with Hor2 approach

O 3.790276601 5.624763031 -2.085730709

C 3.035618525 4.772011459 -2.079610598

Table B.18. Coordinates for CO molecule adsorbed on uranium surface at the center site with Vert1 approach

O 5.227923970 1.691466092 -3.758344100

C 5.227480194 1.687714798 -4.900238140

Table B.19. Coordinates for CO molecule adsorbed on uranium surface at the center site with Vert2 approach

- C 5.227923346 1.690776852 -0.880227615
- O 5.227479431 1.687715977 -2.022087184

Table B.20. Coordinates for CO molecule adsorbed on uranium surface at the center site with Hor1 approach

C 5.800042277 1.0	676646955	-0.822751055
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O 4.658116834 1.702450241 -0.825697489

Table B.21. Coordinates for CO molecule adsorbed on uranium surface at the center site with Hor2 approach

- C 5.628150636 2.125592252 -1.692066085
- O 4.780906949 1.323319299 -1.694849201
APPENDIX C

Z-MATRIX COORDINATES FOR DIFFERENT SILVER CLUSTERS

Table C.1. Coordinates for $Ag_2O_2^-$

Ag1

Ag2 Ag1 r1

O1 Ag2 r2 Ag1 a1

O2 O1 r3 Ag2 a2 Ag1 d

r1=2.75

r2=2.50

r3=1.28

a1=180.0

a2=146.0

d=180.0

Table C.2. Coordinates for Ag₂CO⁻

Ag1

Ag2 Ag1 r1

C Ag2 r2 Ag1 a1

O C r3 Ag2 a2 Ag1 d

r1=2.75

r2=2.15

r3=1.28

a1=180.0

a2=140.0

d=180.0

Table C.3. Coordinates for $Ag_2CO_3^-$

Ag1

C Ag1 r1

O1 C r2 Ag1 a1

Ag2 C r3 O1 a2 Ag1 d1

O2 Ag2 r4 C a3 O1 d2

O3 O2 r5 Ag2 a4 C d2

r1=2.30

r2=1.30

r3=2.30

r4=2.30

- r5=1.30
- a1=120.0
- a2=120.0
- a3=160.0

a4=170.0

d1=180.0

d2=90.0

Table C.4. Coordinates for $Ag_2O_2^+$

Ag1

Ag2 Ag1 r1

O1 Ag2 r2 Ag1 a1

O2 O1 r3 Ag2 a2 Ag1 d

r1=2.75

r2=2.50

r3=1.28

a1=180.0

a2=146.0

d=180.0

Table C.5. Coordinates for Ag_2CO^+

Ag1

Ag2 Ag1 r1

C Ag2 r2 Ag1 a1

O C r3 Ag2 a2 Ag1 d

r1=2.75

r2=2.15

r3=1.28

a1=180.0

a2=140.0

d=180.0

Table C.6. Coordinates for $Ag_2CO_3^+$

Ag1

Ag2 Ag1 r1

O1 Ag1 r2 Ag2 a1

- C O1 r3 Ag1 a2 Ag2 d1
- O2 C r4 O1 a3 Ag1 d2

O3 C r5 O2 a4 Ag1 d2

- r1=2.80
- r2=2.30
- r3=1.30
- r4=1.30
- r5=1.30
- a1=80.0
- a2=100.0
- a3=100.0

a4=100.0

d1=180.0

d2=90.0

Table C.7. Coordinates for Ag_2O_2

Ag1

Ag2 Ag1 r1

O1 Ag2 r2 Ag1 a1

O2 O1 r3 Ag2 a2 Ag1 d

r1=2.75

r2=2.50

r3=1.28

a1=180.0

a2=146.0

d=180.0

Table C.8. Coordinates for Ag₂CO

Ag1

Ag2 Ag1 r1

C Ag2 r2 Ag1 a1

O C r3 Ag2 a2 Ag1 d

r1=2.75

r2=2.15

r3=1.28

a1=180.0

a2=140.0

d=180.0

Table C.9. Coordinates for Ag₂CO₃

Ag1

C Ag1 r1

O1 C r2 Ag1 a1

Ag2 C r3 O1 a2 Ag1 d1

O2 Ag2 r4 C a3 O1 d2

O3 O2 r5 Ag2 a4 C d2

r1=2.30

r2=1.30

r3=2.30

r4=2.30

- r5=1.30
- a1=120.0
- a2=120.0
- a3=150.0

a4=150.0

d1=180.0

d2=9

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