

# Density Functional Theory Study of Ag-Cluster/CO Interactions

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**Abstract.** The interactions between carbon monoxide and small clusters of silver atoms are examined. Optimal geometries of the cluster-molecules complexes, i.e. silver cluster - carbon monoxide molecule, are obtained for different sizes of silver clusters and different numbers of carbon monoxide molecules. This analysis is performed in terms of different binding energy of these complexes and analysis of the frontier orbitals of the complex compared to those of its constituents. The silver atom and the dimer ( $\text{Ag}_2$ ) bond up to three carbon monoxide molecules per Ag atom, while the larger clusters appear to saturate at two CO's per Ag atom. Analysis of the binding energy of each CO molecule to the cluster reveals that the general trend is a decrease with the number of CO molecules, with the exception of Ag where the second CO molecule is the strongest bound. A careful analysis of the frontier orbitals shows that the bent structures of  $\text{AgCO}$  and  $\text{Ag}_2\text{CO}$  are a result from the interaction of the highest occupied orbital of Ag (5s) and  $\text{Ag}_2$  ( $\sigma$ ) with the lowest unoccupied orbital of CO ( $\pi^*$ ). The same bent structure also appears in the bonding of CO to some of the atoms in the larger clusters. Another general trend is that the CO molecules have a tendency to bond atop of an atom rather than on bridge or face sites. These results can help us elucidate the catalytic properties of small silver clusters at the atomic level.

## 1 Introduction

Studies directed at understanding the interaction of metal clusters with molecules remain the subject of active theoretical and experimental studies [1]. The recent shift in the focus of enquiry from the study of the structural and electronic properties of single-component metal clusters to the study of the interaction of metal clusters with molecules is driven in large part by the potential use of metal clusters in heterogeneous catalysis. Clusters have been long known to show size-specific physical and chemical properties that are often at odds with their bulk properties. This size-specific behavior is evident in the catalytic

properties as well, leading to highly reactive clusters whose catalytic behavior is at odds with their bulk counterparts. For example, it has been known for some years now that gold nanoclusters supported on metal oxides such as  $\text{TiO}_2$  can efficiently oxidize carbon dioxide at fairly low temperatures [2]. More recently, the eight atom gold cluster supported on an  $\text{MgO}$  substrate has been shown to be the smallest clusters capable of catalyzing the oxidation of carbon monoxide [3].

The situation for silver clusters is less conclusive. In the bulk and the near bulk regime of several micrometers, silver plays a unique role that is not replicated by any other transition metal in the selective oxidation of ethylene into ethylene oxide, a widely-used industrial catalytic process [4]. Yet, little is known about the details of the mechanism of the oxidation reaction at an atomistic level. There is significant progress of late in experimental techniques that can be used to soft-land clusters on to substrates to perform precise size specific investigations to study the size-specific chemical reactivity of clusters and consequently their catalytic properties. Likewise, advances in first-principles theoretical methods such as density functional theory and quantum chemistry techniques provide another direct route to studying the chemical properties of the clusters at an atomistic level. Since it is as yet unclear as to whether silver clusters exhibit the catalytic oxidation of CO like gold clusters do, it is perhaps not surprising that several theoretical [5,6,7,8,9] and experimental [9,10] investigations have attempted to address the interaction of silver clusters with  $\text{O}_2$  and CO in an attempt to study the fundamental cluster-molecule interaction as the first step towards understanding the larger question of the role, if any, of silver clusters in the catalytic oxidation of CO.

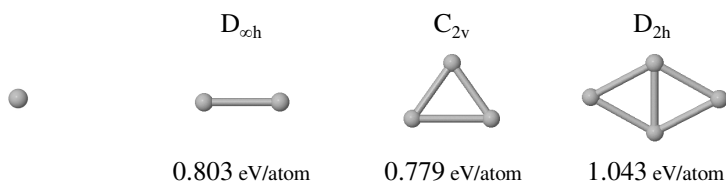
In this paper, we examine the interaction of small silver clusters ( $\text{Ag}_n$ ,  $1 \leq n \leq 4$ ) with one or more CO molecules. The ground (2S) state of the Ag atom is well-separated first excited (2D) state, the d orbitals are localized relative to the 5s orbitals and bonding in the silver clusters is dominated by the 5s electrons. It is not surprising therefore that silver clusters display structural and electronic properties that are quite similar to those of alkali metal clusters. The geometric and electronic properties of pure silver clusters have been well studied [11,12,13,14] and the candidates for the lowest energy structures in the size range of  $n \leq 10$  that is of interest to us are well-elucidated. We study the interaction of the cluster molecules system under the framework of the generalized gradient approximation of the density functional theory. The functionals used in the calculations presented in this paper combine Becke exchange functional [15] with the Perdew-Wang [16] correlation functional as implemented in Gaussian 03 [17]. A 28-electron core ([Ar]3d10) effective core potential is combined with contracted Gaussian-type orbitals for the remaining 19 electrons for the Ag atoms [18]. Carbon and oxygen atoms are represented by the DGTZVP[19] all-electron basis sets as implemented in Gaussian 03 [17]. The selection of pseudopotential and exchange-correlation functionals was made to compare with previous results on the bare clusters as reported in ref. [14] and the choice in that reference was based in tests to reproduce the properties of Ag,  $\text{Ag}_2$  and  $\text{Ag}_3$ . The DGTZVP was chosen to reproduce the experimental binding energy of CO. The

equilibrium structures were obtained using gradient-based methods. The optimizations were performed in all degrees of freedom. Normal mode analysis was performed to determine whether a structure was a minimum or a saddle point in the potential energy surface of the cluster. The starting point was the bare silver cluster structures of ref. [14]. CO molecules were added until saturation was reached. The saturation was 3 CO molecules per Ag atom for the Ag and Ag<sub>2</sub>. Ag<sub>3</sub> and Ag<sub>4</sub> bonded 2 CO molecules per silver atom. The bonding of CO to the cluster is analyzed in terms of the binding energy of CO to the clusters.

## 2 Results

### 2.1 Bare Silver Clusters

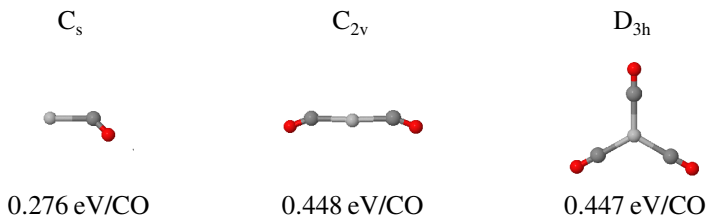
In this subsection we briefly review the properties of small silver clusters as obtained in the previous study of Srinivas *et al.* [14]. In Fig. 1 we present the lowest energy isomers of Ag<sub>n</sub>, n = 1 - 4, and their respective binding energies as obtained in ref. [14] and confirmed by our current results. Ag<sub>4</sub> is a rhombus rather than a tetrahedron which is a common form for tetramers of other elements. A 3-dimensional form will only form for neutral silver clusters containing 7 or more atoms[14]. The binding energy in the range of n ≤ 10 increases, non-monotonically, with the number of atoms in the cluster. In this work we will restrict ourselves to the smaller size clusters (n ≤ 4) as we are more interested in understanding the binding mechanism of carbon monoxide to the bare and CO-rich silver clusters.



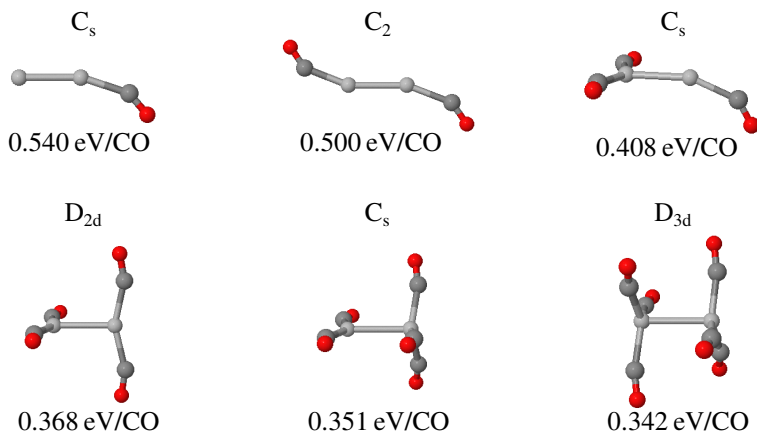
**Fig. 1.** Structure of the most stable isomer of Ag<sub>n</sub>, n = 1 - 4

### 2.2 Ag<sub>N</sub>(CO)<sub>x</sub>

To understand the mechanism and the energetics of the bonding of CO to small silver clusters we begin with the structures presented in Fig. 1 and add CO molecules until they no longer bond to the clusters. This determination is made when the binding energy of the last CO to the previous cluster is negative or zero. In Fig. 2 we present the structure of Ag(CO)<sub>x</sub>, x = 1 - 3. One can see that in both AgCO and Ag(CO)<sub>2</sub> the CO molecule is bent with respect to the Ag-C bond. A careful analysis of the frontier orbitals of both the Ag atom and dimer and of CO shows that the π\* orbital of CO tends to align with the 5s orbital of Ag or the σ orbital of Ag<sub>2</sub>, resulting in the bent structure of Fig. 2. In the following analysis we will consider the binding energy of the CO to the complex Ag(CO)<sub>n-1</sub> as



**Fig. 2.** Structure of  $Ag(CO)_x$ ,  $x = 1 - 3$ . For each structure we present the point group symmetry and the corresponding binding energy per CO ligand. The silver atoms are light grey, the C atoms dark grey and the O are red.



**Fig. 3.** Structure of  $Ag_2(CO)_x$ ,  $x = 1 - 6$ . For each structure we present the point group symmetry and the corresponding binding energy per CO ligand.

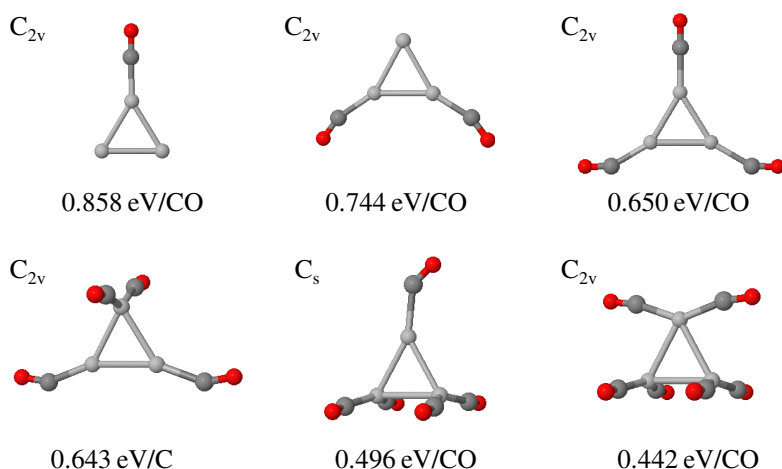
$BE(\text{last CO}) = E(\text{CO}) + E(\text{Ag}(\text{CO})_{n-1}) - E(\text{Ag}(\text{CO})_n)$ . Using this energy we can determine the relative stability of the complex as CO molecules are added. The binding energy of CO to Ag is relatively weak, for the first CO it is about 0.276 eV, it increases for the second CO to 0.619 eV, and then decreases again to 0.446 eV when a third carbon monoxide is added. This explains why the binding energy per CO defined as  $BE(\text{CO}) = [n \times E(\text{CO}) + E(\text{Ag}(\text{CO})) - E(\text{Ag}(\text{CO})_n)]/n$  reported in Fig. 2 for  $Ag(\text{CO})_2$  and  $Ag(\text{CO})_3$  are nearly the same. A fourth CO did not bond to the cluster.  $Ag(\text{CO})_3$  is very symmetric, belonging to the  $D_{3h}$  point symmetry group. This suggests, that although the third CO is weakly bonded, each Ag atom can bond up to 3 CO's.

In Fig. 3 we display the  $Ag_2(\text{CO})_x$ ,  $x = 1 - 6$ , indicating again that although a weakly bonded system, each Ag atom can bond up to 3 carbon monoxide molecules. Just as discussed in the previous paragraph, in all the cases studied for  $Ag_2$  the O atom is not in the same line as the Ag-C bond. A careful analysis of the frontier orbitals once again show us that this is a result of the interaction of the  $\pi^*$  orbital of CO with the orbitals of Ag. The cluster becomes less stable

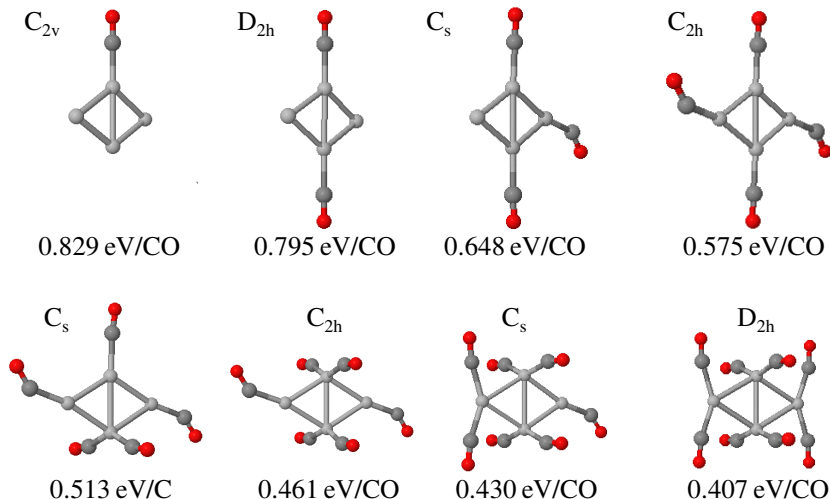
upon addition of CO. However, the smallest binding energy of CO to  $\text{Ag}_2$  is still comparable with the binding of a single CO to the Ag atom.

The structures of the  $\text{Ag}_3(\text{CO})_x$ ,  $x = 1 - 6$  are displayed in Fig. 4. The first thing to note is that in  $\text{Ag}_3(\text{CO})$  and  $\text{Ag}_3(\text{CO})_3$  the top CO is in perfect alignment with the Ag-C bond. In this case the orbitals that interact are the  $\pi^*$  of CO with a  $\pi$ -like orbital of  $\text{Ag}_3$ . However, this trend is not followed for all single CO bonded to Ag, as one can see in the case of  $\text{Ag}_3(\text{CO})_2$ .  $\text{Ag}_3$  bonds up to 2 CO's per Ag atom, something that can be explained by the extra Ag-Ag bond. A possibility of binding 3 CO's per Ag atoms would be as a linear  $\text{Ag}_3$  backbone and each  $\text{Ag}(\text{CO})_3$  stacked in a staggered fashion, as a sandwich cluster. This structure demonstrated to be unstable and we don't think larger sizes will be stable. The binding energy per CO molecule shows a decreasing trend, but like in the case of  $\text{Ag}_2$ , the strength of the weakest CO-Ag bond in  $\text{Ag}_3(\text{CO})_6$  is comparable to the Ag-CO bond in AgCO. In  $\text{Ag}_3(\text{CO})_5$  the 2 CO's bonded to a single Ag atom are perpendicular to the plane of the molecule. While in  $\text{Ag}_3(\text{CO})_6$  the last two CO's are in the same plane as  $\text{Ag}_3$ . One can reason that these are steric effects that will tend to minimize the repulsion between the CO molecules.

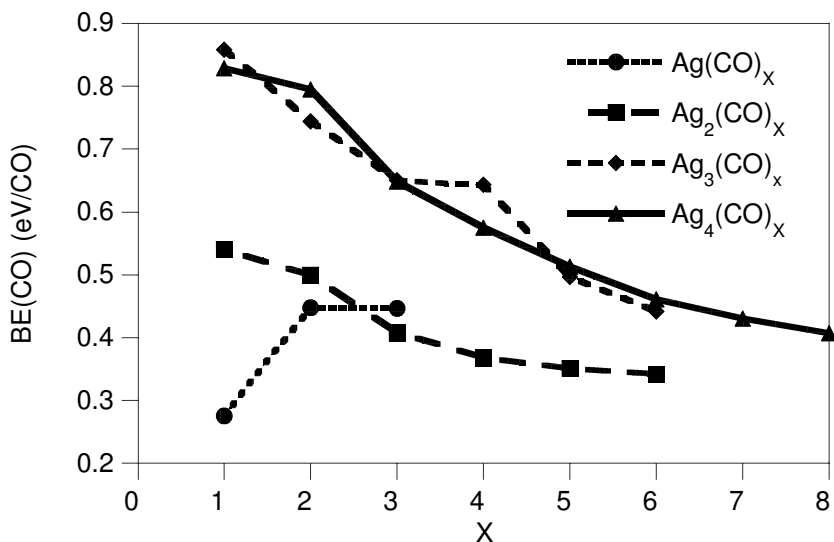
The last set of structures studied in this work is displayed in Fig. 5. Both  $\text{Ag}_4\text{CO}$  and  $\text{Ag}_4(\text{CO})_2$  have the CO molecule aligned with the Ag-CO bond. The explanation is very similar to the one for the case of  $\text{Ag}_3$ . But, due to the higher symmetry of  $\text{Ag}_4$  the second CO bonds in the same fashion as the first. Each Ag atom will bond a single CO atoms before a second CO will bond to it. This was the trend for the smaller sizes as well.  $\text{Ag}_4(\text{CO})_8$  has a very similar structure to  $\text{Ag}_3(\text{CO})_6$ , it consists of two pair of CO molecules bonded in the plane perpendicular to  $\text{Ag}_4$  and two pairs that are parallel to its plane. In the cases explored in this work not a single CO bonded in a face or a bridge site, a fact that can attributed to both the frontier orbitals of CO and  $\text{Ag}_n$ .



**Fig. 4.** Structure of  $\text{Ag}_3(\text{CO})_x$ ,  $x = 1 - 6$ . For each structure we present the point group symmetry and the corresponding binding energy per CO ligand.



**Fig. 5.** Structure of  $\text{Ag}_4(\text{CO})_x$ ,  $x = 1 - 8$ . For each structure we present the point group symmetry and the corresponding binding energy per CO ligand.



**Fig. 6.** The binding energy of CO (per CO ligand) to  $\text{Ag}_N$ ,  $N = 1 - 4$ . The binding energy is computed as  $BE(\text{CO}) = (x \times E(\text{CO}) + E(\text{Ag}_N) - E(\text{Ag}_N(\text{CO})_x))/x$ .

In Fig. 6 we present the binding energy per CO to  $\text{Ag}_n$ ,  $n = 1 - 4$  as a function of the number of CO molecules bonded to the cluster. This quantity is a measure of the stability of the cluster upon addition of ligand molecules. The first thing we learn from Fig. 6 is that the binding energy of CO to  $\text{Ag}_n$  increases with

cluster size. However, as more CO molecules are added the binding energy for all the sizes seem to decrease to approximately the same value. The data in the figure also allow us to conclude that the only case in which the system becomes more stable upon addition of more CO molecules is the Ag atom. This might be understood in terms of the orbitals that are responsible to the formation of the carbon-silver bond. Ag<sub>2</sub>, Ag<sub>3</sub>, and Ag<sub>4</sub> all become less stable upon addition of carbon monoxide. As a consequence at high temperatures one might only observe Ag<sub>N</sub>CO. Nevertheless, in low temperature conditions or in clusters deposited on a substrate there is a possibility that these CO-rich clusters might form and play a role in the reactions involving carbon monoxide.

### 3 Concluding Remarks

In this work we studied the structural properties and the interaction of carbon monoxide with silver clusters. We conclude that low coordination Ag atoms can bond up to 3 CO's, being the last CO molecule only weakly bonded. Analysis of the frontier orbitals explains why in many cases that CO molecule is not aligned with the Ag-C bond. The binding energy per CO molecule decreases with the number of CO molecules bonded to the cluster, the only exception is the Ag atom where the second CO molecule is more strongly bonded than the first. Steric effects explain the structure of the saturated clusters. Ag<sub>2</sub>(CO)<sub>6</sub> consists of two Ag(CO)<sub>3</sub> structures staggered in a D<sub>3d</sub> arrangement. While Ag<sub>3</sub>(CO)<sub>6</sub> has two pairs of CO molecules bonded perpendicular to the plane of Ag<sub>3</sub> and the 3rd pair is parallel. A similar situation is seen in Ag<sub>4</sub>(CO)<sub>8</sub> where two pairs are perpendicular and two pairs are parallel to the plane of Ag<sub>4</sub>.

We speculate that the likely saturation of the planar Ag<sub>5</sub> and Ag<sub>6</sub> clusters to be 10 and 12 pairs of CO molecules bonded in patterns similar to the ones for Ag<sub>3</sub> and Ag<sub>4</sub>. On the other hand, for the tridimensional structures the saturation point may be a single CO molecule per surface atom due to their higher coordination. Future work will be to extend this work to larger size clusters and to explore the electronic properties of neutral and charged clusters. In addition, we would like to explore other ligands and study catalytic properties of small silver clusters in the gas phase as well as of silver clusters deposited on a substrate.

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