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Density Functional Study of the Interaction of Carbon Monoxide with Small Neutral and Charged Silver Clusters

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CO adsorption on small neutral, anionic, and cationic silver clusters Ag_n ($n = 1-7$) has been studied with use of the PW91PW91 density functional theory (DFT) method. The adsorption of CO on-top site, among various possible sites, is energetically preferred irrespective of the charge state of the silver cluster. The cationic silver clusters generally have a greater tendency to adsorb CO than the anionic and neutral silver ones, except for $n = 3$ and 4, and the binding energies reach a local minimum at $n = 5$. The binding energies on the neutral clusters, instead, reach a local maximum at $n = 3$, which is about 0.87 eV, probably large enough to be captured in the experiments. Binding of CO to the silver clusters is generally weaker than that to the copper and gold counterparts at the same size and charge state. This is due to the weaker orbital interaction between silver and CO, which is caused by the larger atomic radius of the silver atom. In contrast, Au atoms with a larger nuclear charge but a similar atomic radius to silver owing to the lanthanide contraction are able to have a stronger interaction with CO.

I. Introduction

In the past few years, atomic and molecular chemisorptions on small metal clusters in the gas phase have attracted considerable attention, both experimentally and theoretically.[1] Physical and chemical properties of small clusters are usually very different from those of the corresponding bulk material. Recent advances have provided the practical usage of metal clusters as catalysts.[2] CO is one of the most useful monocarbon molecules and yet one of the most common byproducts in many reactions, and its reactions with metal clusters have been extensively studied,[3−8] both for probing the electronic structure of the clusters and finding promising catalysts to convert CO to various compounds.

Stimulated by the recent findings that gold nanoparticles exhibit high CO oxidation activity, an increasing number of studies, both experimentally and theoretically, have put great effort into determining the chemical properties of the pure and supported gold clusters/nanoparticles, especially their interaction with CO.[6−14] Besides gold, the interactions of CO with copper[10−20] and silver[10,11,21−26] clusters/nanoparticles, and the binary silver−gold clusters/nanparticles[9,27,28] have also drawn remarkable attention. Silver has the same electron configuration as copper and gold: all have a closed d shell and a single s valence electron, which can be seen as “alkali-like” metals.[29] Therefore it is natural to anticipate that silver clusters may have similar properties as copper and gold clusters. However, both theoretical calculations on MCO (M = Cu, Ag, Au),[11] $AgCO^+$,[30,31] and Ag_2CO^- [21] and experimental studies[10,24,32] found that the interaction of CO with a silver atom and clusters is significantly weaker than that with the other two with the same size. On the other hand, the interaction of the silver atom and clusters with CO is also as strongly affected by the charge state of the atom and clusters as the other two. Ag_nCO^- are the least stable silver carbonyls, and none of them have been observed in the experiments.[10,24] Neutral Ag_nCO are a little more stable. $Ag(CO)_m$ ($m = 2$, 3) complexes seem to be detected only in matrix isolation at low temperature.[33−35] Ag_2 was found not to react with CO,[32] and larger neutral $Ag_n(CO)_m$ complexes are only reported in the presence of excessive CO such as in the CO droplet.[25,26] By contrast, positively charged silver atoms and clusters bind more strongly with CO and $Ag_n(CO)_m^+$ complexes are much easier to capture and then study by various experiments.[26,27,31,36−39]

As indicated by the experimental and theoretical studies, the adsorptions of CO on the copper and gold clusters are both affected by the cluster size and charge states of the clusters. However, much less effort has been expended for the size dependence of the interaction of the silver clusters with CO. Despite the massive experimental efforts on the interaction of Ag_n clusters with CO, there are just a few theoretical studies on the interaction of silver atom or dimer with CO.[11,21,29,31] Here, we present a systematic theoretical study of the binding of a CO molecule with small neutral and charged Ag_n ($n \leq 7$) clusters with DFT methods in hopes of understanding the bonding nature between the silver clusters and CO, clarifying the previous experiments and including predictions that have not been previously studied.

II. Computational Methods

Density functional theory techniques with generalized gradient approximation (GGA) for exchange-correlation potential presently seem to be the most powerful tool to deal with the metal clusters. One of the most important involvements in these DFT calculations is the choice of the exchange and correlation functionals. The recent DFT study related to bare silver clusters with different functionals shows that B3LYP, BLYP, and G96LYP functionals can be considered as incorrect in predicting the most stable structures of certain small silver clusters.[40] Our group has tested the accuracies of DFT methods by comparing

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the DFT calculation results with those of coupled cluster theory and experimental data.[41] The results indicate that the accuracy of the DFT results is highly dependent upon the functional employed and the PW91PW91[42,43] functional was found to have some advantages. Therefore, in this work, the PW91PW91 functional was employed for all the calculations. The basis sets LANL2DZ and the corresponding Los Alamos relativistic effective core potential (RECP) were used to take into account scalar relativistic effects, including mass velocity and Darwin correction, for the heavy silver atom. For C and O atoms, the all electron basis set 6-311G(d) was employed. In a previous study of CO with gold clusters, it was found that the binding energy, bond length, and vibrational frequency of the CO molecule calculated with this method agree well with the experimental values.[44] Moreover, the LANL2DZ basis set with three additional *f*-type polarization functions[45,46] for Ag atoms and 6-311+G (3df) for C and O atoms were used for more precise single-point-energy calculation. All binding energies were corrected with basis set superposition error (BSSE) estimated by using the counterpoise corrections method.[47] The binding energy is defined by the following equation:

$$E_{\mathrm{b}} = (E_{\mathrm{Ag\ cluster}} + E_{\mathrm{CO}}) - E_{\mathrm{complex}} \tag{1}$$

The more positive the E_{b} is, the stronger the bond is.

All the calculations were performed with the Gaussian 03 suite of programs.[48] For each structure, the stable method[49,50] as implemented in the Gaussian 03 was used to establish a stable wave function. Vibrational frequency calculations were performed to guarantee the optimized structures are local minima and provide zero-point (ZPE) energy. Natural bond orbital (NBO)[51] analyses were performed to understand the bonding in these molecules.

III. Results and Discussion

A. Structures and Stability. To study the adsorption of CO on the silver clusters, for each cluster size and each charge state, a great number of possible structures were searched and optimized. A few of the low-energy structures of complex clusters are shown in Figures 1−3 (more structures can be seen in the Supporting Information for the conciseness of the text[52]), and the binding energies are also given. The most stable silver clusters taken from ref 53 are listed on the left in Figures 1−3. Figures 1−3 indicate that the most stable structures of complex clusters are all with the carbon on-top binding to the silver clusters, irrespective of the charge state, and lie 0.50 eV or more below other binding configurations including those of bridge and hollow sites. This adsorption configuration is the same as the carbon monoxide adsorption on small copper[54] and gold clusters,[44,55] and could be easily illustrated with their unique "alkali-like" electronic configurations. There have been some interpretations on the selective CO adsorption sites on the gold and copper clusters[54,55] in previous studies. The similar valence electron configuration of the silver, along with its weak back-donation to the CO, also reduces the stability and possibility of the CO bridge and hollow adsorption on the silver clusters, which is significantly different from that of other transition metals.

For the monomer complexes, $AgCO^+$ ($^1\Sigma$) which has the largest binding energy is linear, while both AgCO ($^2A'$) and $AgCO^-$ ($^1A'$) have a bent structure, similar to that of the AuCO[11] complexes. CuCO is linear at the MP2 level[11] and the PW91PW91 level, which is in agreement with the experimental studies,[12,18] and slightly different from the structure of the AgCO and AuCO complexes. This bent AgCO structure can be elucidated by considering the orbital interaction between the CO molecule and the silver atom. The frontier molecular orbitals of CO are 5σ as highest occupied molecular orbital (HOMO) and 2π as lowest unoccupied molecular orbital (LUMO), which are −0.329 and −0.069 au at the PW91PW91/LANL2DZ level, respectively. They are both concentrated on the carbon site. For the Ag atom, the frontier orbitals are 4d (SOMO-1, full occupied), 5s (SOMO, single occupied molecular orbital, half occupied), and 5p (SOMO+1, unoccupied). For the binding of the Ag atom with CO, the possible combinations of the frontier orbitals which may gain energy are 4d to 2π (0.212 au), 5s to 5σ (0.154 au), and 5p to 1π (0.394 au) for the linear conformer, while they are 5s to 1π (0.255 au) and 5s to 2π (0.105 au) for the bent conformer, where the value in parentheses is the absolute energy difference between the two orbitals. Obviously, the energy favorable combination is the 5s to 2π in the bent conformer. Although the 5s to 5σ combination is just about 0.05 au unfavorable, since the metal s orbital is spherical, the 5s and 5σ orbitals can still overlap in a bent structure. Thus, the AgCO complex prefers a bent structure.

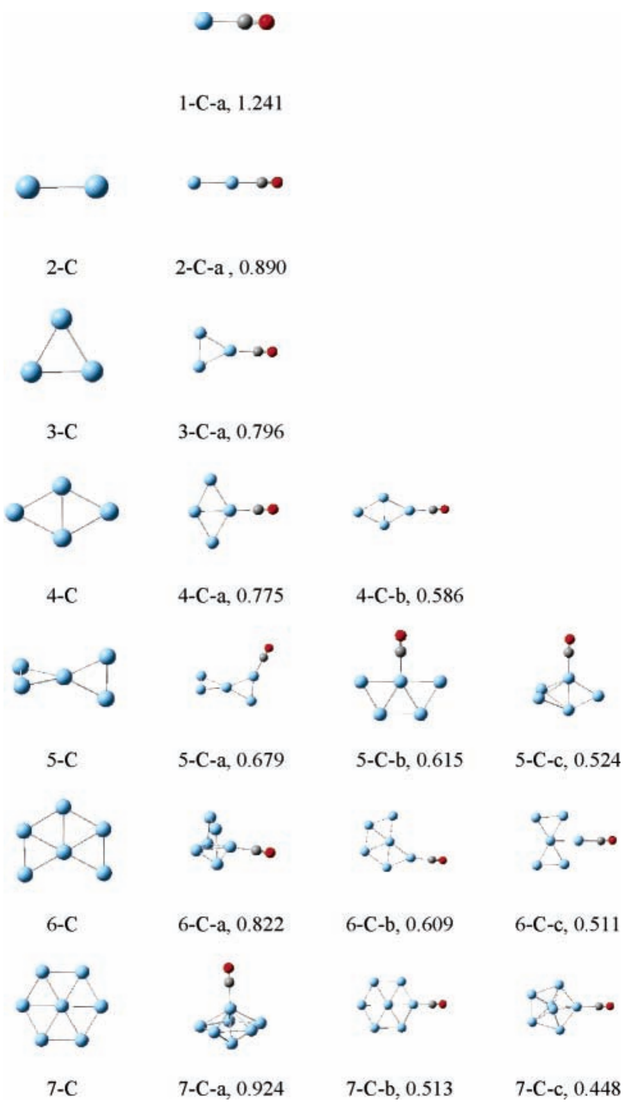

Figure 1. Low-energy structures of Ag_nCO^+. The ground-state structures of the corresponding bare cationic silver clusters are given on the left. Binding energy is given in eV.

For the Ag_2CO and its charged counterparts, the cationic complex has a linear geometry while the neutral and anionic

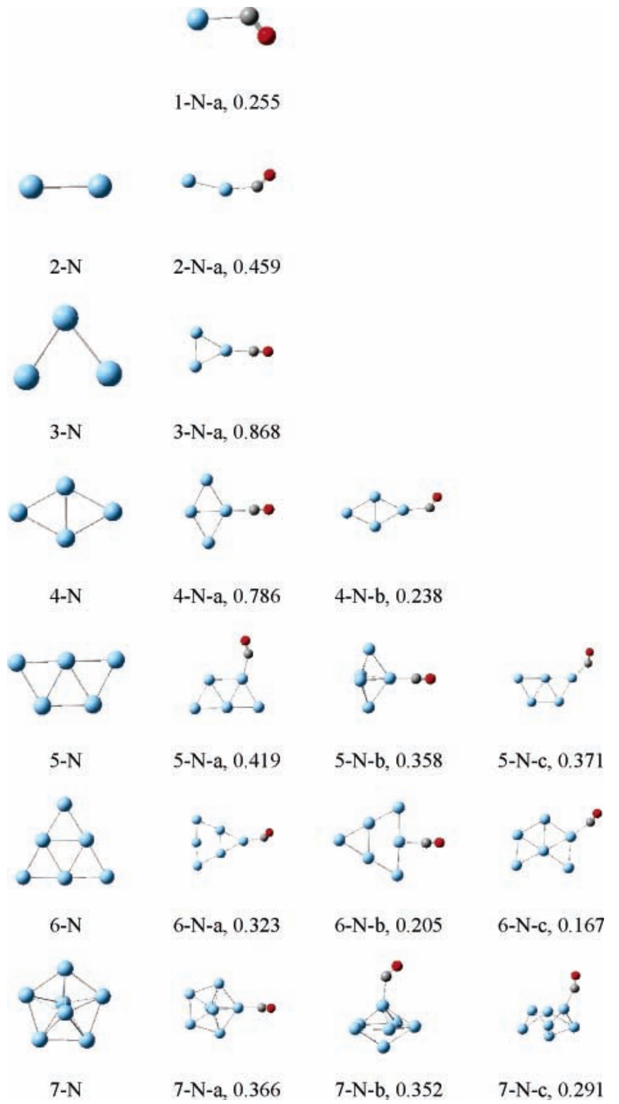

Figure 2. Low-energy structures of Ag_nCO. The ground-state structures of the corresponding bare neutral silver clusters are given on the left. Binding energy is given in eV.

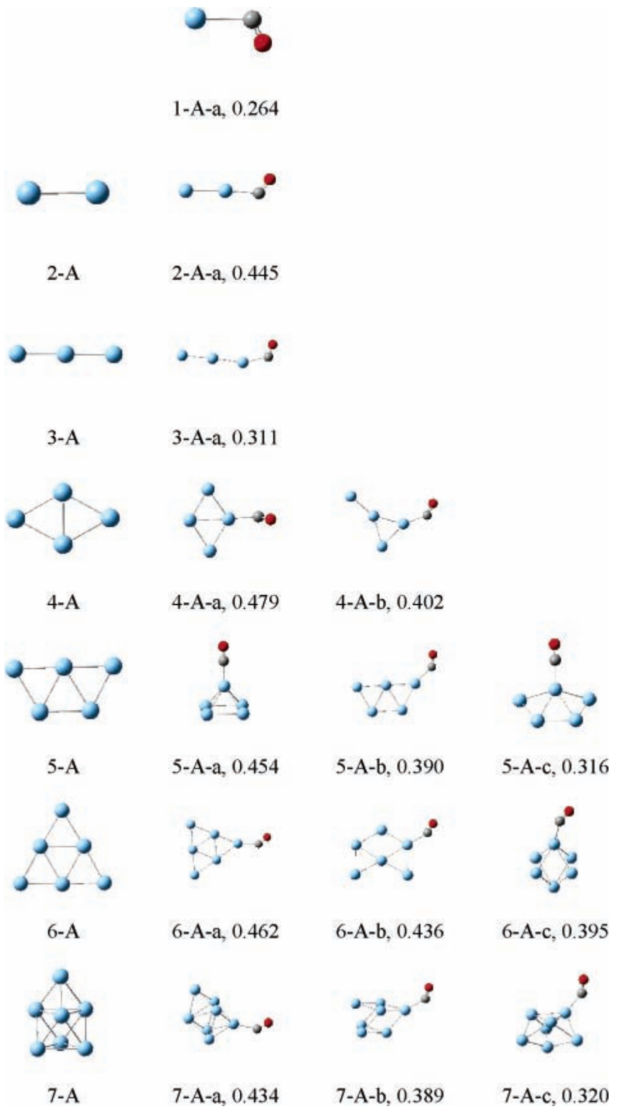

Figure 3. Low-energy structures of Ag_nCO^-. The ground-state structures of the corresponding bare anionic silver clusters are given on the left. Binding energy is given in eV.

ones have tilted structures, showing a similar binding pattern as in the monomer complexes. The structure of Ag_2CO^- is similar to the available theoretical result[21] and the binding energy is also in good agreement with the value of 0.49 eV in ref 21. The interactions of Ag_2, Ag_2^+, and Ag_2^- with CO are rather weak. The distances between the silver clusters and carbon monoxide remain within the range from 2.1 to 2.3 Å. For the Ag_3CO complexes, both the cationic and neutral complexes have C_{2v} geometry while the C_{2v} structure for the anionic complex is a second-order transition state. The most stable anionic complex with C_s symmetry again has the smallest binding energy among the three.

The number of possible adsorption structures increases rapidly with the growth in cluster size. From $n = 4$ on, only the isomers with energy close to the lowest one are listed. For $n = 4$, the cationic and neutral complexes both have C_{2v} geometry while that of the anion only has C_s geometry due to the departure of CO from the Ag_4 plane. The CO molecule still prefers the on-top adsorption site for $n = 5$. However, it is interesting to notice that from $n = 5$ on, the most stable structures are not always obtained from the most stable silver clusters. The Ag_5CO^- is an obvious example. The bare Ag_5^- with C_{4v} symmetry lies higher in energy than the most stable Ag_5^- with C_{2v} symmetry, but the adsorption of the CO molecule does reduce the energy of the whole complex significantly and leads to the most stable geometry **5-A-a** with C_{4v} symmetry.

For $n = 6$, a similar phenomenon to that of Ag_5CO^- also happens to Ag_6CO^+. The energy difference between the two most stable bare Ag_6^+ is just 0.05 eV. After adsorption of a CO molecule, the second stable Ag_6^+ leads to the most stable complex **6-C-a**. The neutral and anionic complexes both have C_s symmetry and are from similar bare D_{3h} structures. However, it is remarkable that the CO molecule is in the same plane of the silver cluster in the anionic complex, while out of the plane in the neutral complex.

The most stable Ag_7CO complexes with different charges are all three-dimensional (3D) structures. Actually, from $n = 5$ on, more 3D structures appear as the most stable geometries of the silver cluster monocarbonyls. This is very different from the gold counterparts, whose most stable complexes are all 2D or quasi-2D.[44,55] The fact that there are more 3D structures in the silver clusters than in the gold clusters is related with the stronger metallicity of silver than gold.

B. Energetics. The binding energies of CO to silver clusters as a function of cluster size for the neutral and charged silver cluster monocarbonyls are plotted in Figure 4. In particular, the

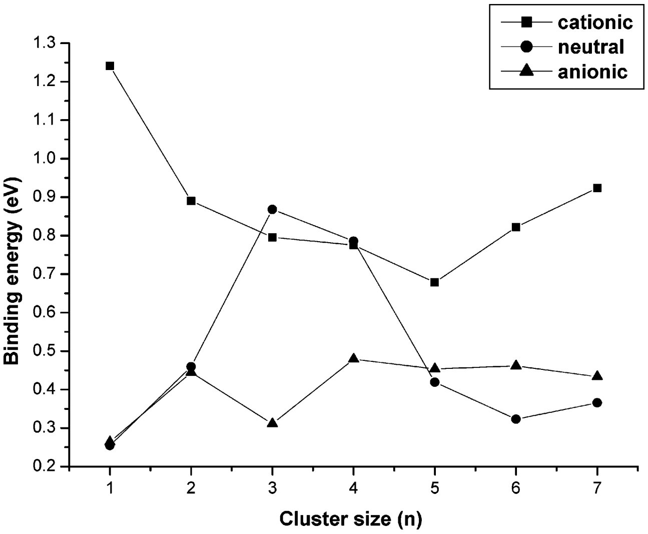

Figure 4. Binding energies as a function of cluster size for Ag_nCO^+, Ag_nCO, and Ag_nCO^-.

binding energy for the cations decreases with cluster size n increasing until $n = 5$ and increases at $n = 6$ and 7. For the neutral complexes the binding energy has a peak at $n = 3$ and a valley at $n = 6$. For the anions, the binding energy has a clear odd−even alternation pattern and becomes weak beyond $n = 4$, in which the binding energy at the even point is larger than its neighbors. This feature is common to the copper group clusters, where the binding energies of CO reach a maximum at $n = 5$ on Cu_n[54] but at $n = 4$ on Au_n.[44,55] It is interesting to note that when $n = 5$, 6, and 7, the neutral Ag_nCO even have the lowest binding energies. However, they may increase again like the trend for Cu_nCO[54]and Au_nCO[55] and probably they can be higher than those of the anions.

The binding energies for the anions with various sizes are all below 0.5 eV, therefore it would be very difficult for the anionic silver clusters to react with CO molecule under the normal condition. Remarkably, the binding energy for the cations is clearly larger than that of the neutral and anionic counterparts except for $n = 3$ and 4, indicating that they can be easily captured in experiments. For the neutrals, except for $n = 3$ and 4, the binding energies are also below 0.5 eV, making it difficult for the experimental to capture these complexes, but not harder than anions. These results are in good agreement with the available experiments which are mentioned in the Introduction. Strikingly, for the neutral Ag_nCO complexes, the binding energies for $n = 3$ and 4, which are 0.87 and 0.79 eV, respectively, are even larger than those of the cation counterparts and larger than those of some Cu_nCO and Au_nCO complexes, for example, CuCO (0.34 eV),[11] Cu_2CO (0.61 eV),[54] and AuCO (0.80 eV).[44] One may expect that Ag_3CO and Ag_4CO may be easier to prepare and capture by the experiments than other sized neutral Ag_nCO complexes.

The binding energies between Ag monomers and CO are smaller than their copper and gold counterparts,[11] although they all have the same valence electron configuration. Generally, the binding energy between CO and metal atoms decreases in the same group as the atomic number increases, due to an increase in the atomic radii of the metal atoms. However, because of the lanthanide contraction, the trend may reverse.[11] The lanthanide contraction makes the gold atom have a very close covalent radius to the silver, but with an extremely larger nuclear charge. The larger nuclear charge then leads to a stronger charge-dipole and dispersion interaction with carbon monoxide. Another factor is the orbital interaction between the metal atomic orbitals and the CO frontier orbitals when forming the bonding MOs in the complex. At the PW91PW91/LANL2DZ level, the energy levels of the valence d and s orbitals are −0.176 and −0.172 au for Cu; −0.282 and −0.175 au for Ag; and −0.270 and −0.230 au for Au, respectively. It can be seen that the Cu 3d is higher in energy than the Ag 4d, thus a better energy match between the d orbitals and the empty valence orbitals of CO may result. Our calculations on CuCO show that there is significant overlap between the Cu 3d orbitals and the CO 2π orbitals in the linear CuCO complex, whereas there is none in the linear AgCO complex. As for Au, its 6s is lower in energy than the Ag 5s while the d orbitals are close in energy, thus a better energy match between the Au 6s orbital and the low lying 1π or 5σ orbital of CO may result (remembering that the valence s orbital of the metal atoms is half filled, the forming MOs may still gain in energy). As a result of both effects, the bond distance of 2.0 Å[44] between the gold atom and the carbon atom of CO is even shorter than that of 2.1 Å in the AgCO complex.

Compared with Cu_nCO[54] and Au_nCO[44,55] complexes, the binding energies for Ag_nCO are usually much smaller at the same size for each charge state. As indicated by the atomic energy levels of the three atoms, Cu has the highest valence d orbital, and Au has the lowest valence s orbital. In the clusters, it is then expected that Cu_n has the highest d band orbitals and Au_n has the lowest s band orbitals for the clusters with the same size and charge state. Ag_n clusters thus have the largest d−s band gap.[56] Therefore, in the Cu_nCO complexes, the d−π back-donation bond is stronger than that in Ag_nCO, while the s−5σ and s−2π orbital interactions are similar. In addition Ag has a larger atomic radius, which makes the electrostatic charge-dipole and dispersion interaction[11,27] in Ag_nCO weaker. On the other hand, in the Au_nCO complexes, the s−5σ bond is stronger, while the d−π back-donation and s−2π bond is weaker. Moreover, due to the lanthanide contraction, the electrostatic charge-dipole and dispersion interaction (dominating interaction in $Au(CO)_m$ complexes)[27,57] in Au_nCO is stronger. As a result, Ag_nCO complexes usually have the weakest CO binding energies.

C. Charge Transfer and C−O Bond Strength. To further understand the interaction between the silver clusters and the CO molecule, natural bond orbital (NBO) population analyses[51] have been performed. Table 1 lists the NBO charges of the CO molecule, C−O vibrational frequencies, and bond lengths of C−O and Ag−CO for the lowest energy complexes shown in Figures 1−3.

For the cations, the silver cationic clusters are electron receptors. The loss of electrons for the CO molecule makes the C−O vibrational frequencies larger and the C−O lengths shorter than those in the free CO molecule, which is undesirable for the activation of the CO bond. For the anions, the silver anionic clusters are electron donators. The CO molecule receives the additional negative charges and this makes its vibrational frequency smaller and the bond length longer, respectively. The results of neutral counterparts are in the middle between those of the cations and the anions. In the neutral complexes, CO draws electrons from the neutral silver clusters. It is interesting to note that the amount of charge transfer between the CO and the neutral/anionic silver clusters follows a clear odd−even alternation pattern. Electron transfer between the metal atom and the CO ligand is a very important stabilizing factor for the bonding between neutral atoms and the CO ligand,[18] since it brings electrostatic attraction between the partially charged atoms or charge-dipole interaction. However, it seems that for the neutrals, electrostatic interaction is not the dominating

TABLE 1: NBO Charges of the CO Molecule, C−O Vibrational Frequencies (cm^{-1}), and Bond Lengths of C−O and Ag−CO (Å) in the Lowest Energy Complexes[a]

species	q_{C-O}	v_{C-O}	R_{C-O}	R_{Ag-CO}
1-C-a	0.094	2230.0	1.126	2.158
2-C-a	0.090	2210.0	1.128	2.188
3-C-a	0.099	2198.3	1.130	2.198
4-C-a	0.067	2169.7	1.132	2.174
5-C-a	0.083	2182.5	1.131	2.189
6-C-a	0.037	2143.1	1.135	2.115
7-C-a	0.029	2138.7	1.135	2.101
1-N-a	−0.141	1999.2	1.151	2.264
2-N-a	−0.042	2075.5	1.143	2.177
3-N-a	−0.102	2034.6	1.146	2.102
4-N-a	−0.062	2073.3	1.143	2.096
5-N-a	−0.095	2031.1	1.146	2.182
6-N-a	−0.045	2065.6	1.143	2.246
7-N-a	−0.066	2052.9	1.144	2.208
1-A-a	−0.301	1882.5	1.168	2.534
2-A-a	−0.387	1819.3	1.177	2.286
3-A-a	−0.226	1928.1	1.161	2.300
4-A-a	−0.309	1872.4	1.168	2.214
5-A-a	−0.214	1973.6	1.157	2.046
6-A-a	−0.305	1878.8	1.167	2.205
7-A-a	−0.204	1953.1	1.157	2.178

[a] For the free CO molecule the calculated vibrational frequency is 2140.4 cm^{-1} and the C−O bond length is 1.137 Å.

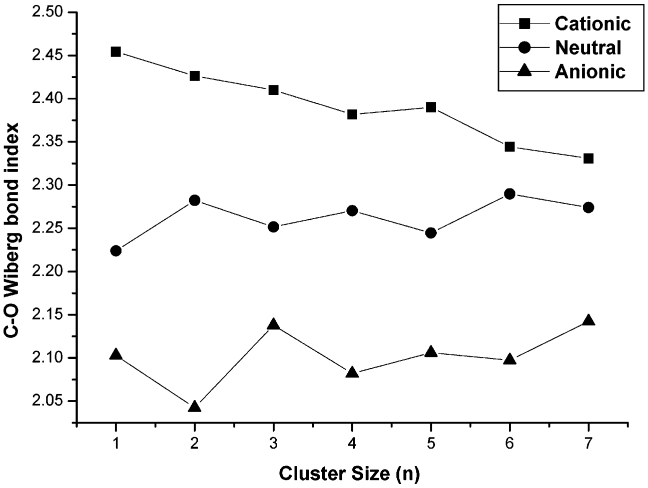

Figure 5. The C−O bond order of CO in the complexes as a function of cluster size.

stabilizing factor, because the binding energies do not follow an odd−even alternation pattern.

The Wiberg bond index is also used to study the C−O bond strength. The results are shown in Figure 5. The Wiberg C−O bond index in the free CO molecule is 2.317. It is clear that the C−O bonds in the neutral and anionic complexes are weakened, while in the cations, all the C−O bonds are strengthened. The changes of the C−O bond order are always related to the charge transfer. When the CO molecule obtains the additional electrons, the C−O bond weakens, and vice versa. In the cationic complexes, CO offers electrons to the cationic silver clusters and the C−O bond strengthens. However, the strength of the C−O bond in the cations almost becomes weaker and weaker with the increase of the silver cluster size except for $n = 5$. Following by this trend, one can expect that the C−O bond order would be equal to that of the free CO molecule when the cluster size is large enough, namely, when positive charge density vanishes.

For the neutral and anionic complexes, the C−O bond strength follows the odd−even alternation pattern. Interestingly, when the anionic complexes reach the peak, the neutral ones reach the valley. The silver cluster with the unpaired electron is more inclinable to donate the excess electron to the LUMO of the CO molecule than its neighbors with the closed shell. As a result, it can weaken the C−O bond to a greater extent. This can also be confirmed by the trend of the charges transferred to the CO molecule. It also can be seen that the C−O bond weakens more in the anionic complexes since the CO molecule obtains more electrons from the Ag$_n$ anions. The changes of C−O vibrational frequencies and bond lengths also reveal the same bonding pattern.

IV. Conclusions

We have presented a systematic study on the interaction of the CO with small neutral and charged silver clusters in the size range of one to seven silver atoms. It was found that CO adsorbed on small silver clusters prefers the on-top site, and adsorption on the most stable bare silver clusters does not always result in the lowest energy complexes.

For small clusters, in addition, charge state is found to have a strong influence on the adsorption configurations. Cationic silver clusters often have bigger binding energies of the CO molecule than the neutral and anionic ones. For the neutral silver clusters, the binding energy with different sizes clearly has a maximum at $n = 3$. The binding energy of anionic complexes has an odd−even alternation behavior, and with the increase of cluster size the oscillating magnitude becomes small. Remarkably, the binding energies of the silver clusters are generally smaller than those of the gold and copper ones. This unusual phenomenon is due to the lanthanide contraction and the distinct interactions between them and CO, correspondingly. Our calculation results show a very good agreement with the available experimental and theoretical results, and predict others that were not previously studied.

NBO analyses show that the cationic silver clusters are electron acceptors, while the neutral and anionic silver clusters are electron donators. The C−O bond is strengthened in the cations and weakened in the neutral and anionic complexes. This is confirmed by the changes of C−O frequency and bond length as well. The unpaired electron of the neutral and anionic silver clusters is also investigated to see if it is the main factor of the charge transfer of the CO molecule.

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Supporting Information Available: Tables of net atomic charges of the adsorbates, zero-point vibrational energies (ZPE), electronic energies (E_e), and $\langle S^2 \rangle$ for the neutral and charged Ag$_n$CO ($n = 1-7$) clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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