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Density Functional Study of Small Neutral and Charged Silver Cluster Hydrides

Shuang Zhao, Zhi-Pan Liu, Zhen-Hua Li, Wen-Ning Wang, and Kang-Nian Fan*

Shanghai Key Laboratory of Molecular Catalysis & Innovative Materials, Department of Chemistry, Center for Theoretical Chemical Physics, Fudan University, Shanghai 200433, China

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Small neutral, anionic, and cationic silver cluster hydrides Ag_nH and anionic HAg_nH ($n = 1-7$) have been studied using the PW91PW91 density functional method. It was found that the most stable structure of the Ag_nH complex (neutral or charged) does not always come from that of the lowest energy bare silver cluster plus an attached H atom. Among various possible adsorption sites, the bridge site is energetically preferred for the cationic and most cases of neutral Ag_n. For anionic Ag_n, the top site is preferred for smaller Ag_n within $n \leq 4$ while the bridge site is preferred for bigger clusters. After binding of the second H atom, the obtained lowest energy structures HAg_nH^- are those with two H atoms shared with only one Ag atom in anionic clusters. Natural bond orbital analysis shows that, irrespective of the charge state, electrons always transfer from silver atoms to adsorbate. Significant odd−even alternation patterns that hydrogen atoms bind more strongly with odd-electron bare clusters than with even-electron bare clusters can be observed.

Introduction

Recently there has been a growing interest in silver cluster hydrides formed in silver-exchange zeolites. Metallic and cationic Ag clusters in zeolites are often composed of 2−8 Ag atoms. There have been few reports demonstrating the reduction behavior of silver cations and the chemistry of the silver species in zeolites.[1−7] Baba and co-workers have presented unequivocal evidence that silver hydride species can be formed through the heterolytic dissociation of H−H over Ag_n^+ in Ag−A and Ag−Y zeolite as

$$ZO^-Ag_n{}^+ + H_2 \rightarrow Ag_n{-}H + ZOH$$

where ZOH represents the Bronsted acid site.[1−3] Moreover, the heterolytic cleavage of a C−H bond of CH_4 proceeding on Ag−Y zeolite can also produce the Ag_n−H species as[7]

$$ZO^-Ag_n{}^+ + CH_4 \rightarrow Ag_n{-}H + ZO^{\delta}{-}CH_3{}^{\delta+}$$

More recently, the formation of Ag_3−H has been established by H MAS NMR spectroscopy, and other unidentified Ag_n−H species have also been observed in experiment.[3,7] However, even the sizes of those silver cluster hydrides that could be generated in the process are not well determined, because unambiguously determining the structure of a small atomic cluster such as the most preferred adsorption site is an almost impossible task for experiments alone.

Theoretical studies on the binding of a hydrogen atom on neutral and cationic Ag clusters have also appeared. The bond length and vibrations of the AgH diatomic molecule have been studied by both experiment and theory in detail.[8,9] The geometries of silver cluster hydrides Ag_nH ($n = 2-5$) have been studied by DFT calculations, and the results show that the framework of the silver cluster in the complexes maintains a geometry similar to that of the original neutral silver clusters.[10] Khairallah and co-workers investigated the gas-phase synthesis and reactivity of Ag_n^+ and $Ag_{n-1}H^+$ and theoretically determined the structures of Ag_2H^+, Ag_4H^+, and Ag_6H^+ by replacing one Ag atom in the bare cluster by a hydrogen atom.[11] They found that the $Ag_{n-1}H^+$ clusters are only slightly less stable than their silver counterparts and have structural features similar to those of Ag_n^+.

However, no detailed study about the adsorption patterns and adsorption structures of anionic silver cluster hydrides has been reported to our knowledge. Even the hydrogen binding energies have not been well determined. A systematic theoretical study of the H interaction with silver clusters is still lacking. Here, we present a systematic theoretical study of the H interaction with silver clusters using density functional theory (DFT). The adsorption of one hydrogen atom on both the neutral and charged Ag_n clusters and two hydrogen atoms on anionic Ag_n clusters ($1 \leq n \leq 7$) has been studied. The structures of the silver cluster hydrides were fully optimized. The binding energies, charge transfer, and vibrational frequency were analyzed to understand the bonding nature between the hydrogen atoms and the silver clusters.

Theoretical Methods

The calculations are carried out using DFT with the generalized gradient approximation (GGA) implemented in the GAUSSIAN 03 package.[12] Recently, the performances of 23 DFT methods have been evaluated on the small neutral and charged Ag_n clusters with $n \leq 4$.[13] The results indicate that DFT methods incorporating Perdew's correlation functionals generally perform better than the other DFT methods incorporating the LYP correlation functional, and PW91PW91[14] is one of the best functions on energetic properties and vibrational frequencies. Consistent with the previous study[15] on Ag_nCl systems, the PW91PW91 DFT method in conjunction with the LANL2DZ basis set and the corresponding Los Alamos relativistic effective core potential (RECP)[16] on Ag atoms and the 6-311++G(d,p) basis set on hydrogen atoms was used. To verify the basis set used in the present study, we have performed calculations on

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* To whom correspondence should be addressed. E-mail: knfan@fudan.edu.cn. Phone and fax: 86-21-65643977.

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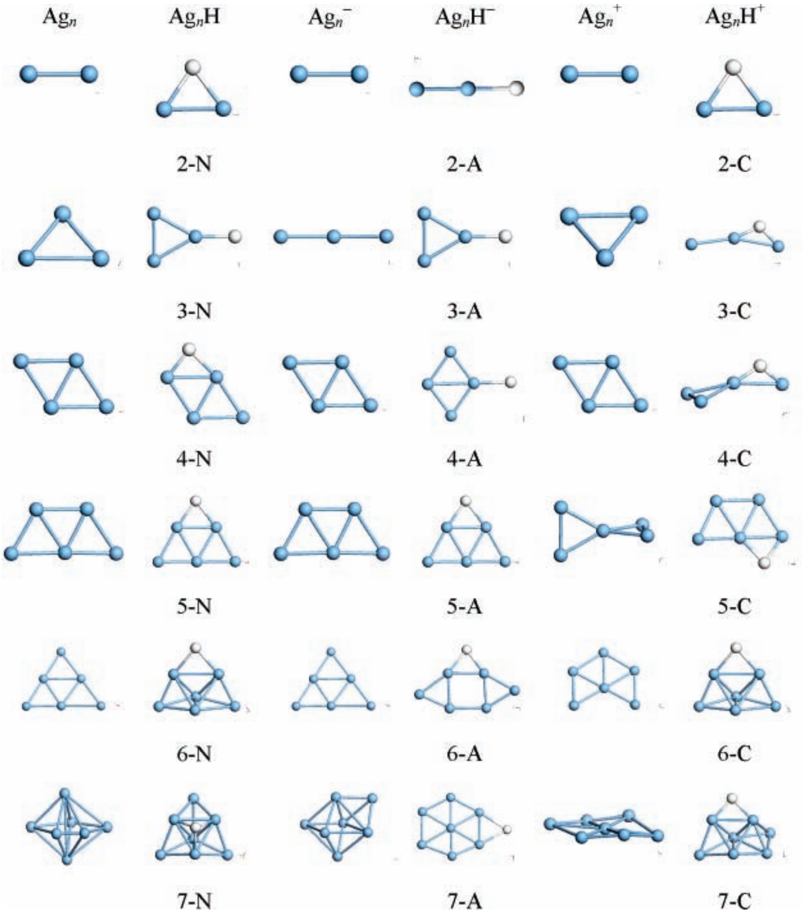


Figure 1. Optimized geometries of the most stable Ag_n, Ag_n^-, Ag_n^+, Ag_nH, Ag_nH^- and Ag_nH^+, $2 \leq n \leq 7$.

AgH^-, Ag_2H^-, $HAgH^-$, and HAg_2H^-, including three additional polarization basis functions (optimized for CCSD) (f, 2.54, 0.73; g, 1.58) and two additional diffuse basis functions (f, 0.2; g, 0.5) with the LANl2DZ basis set for Ag.[17] The calculated binding energies are just 0.02−0.03 eV larger than the results calculated without the diffuse and polarization basis functions. The IP_v (vertical ionization potential) of Ag_n and VDE (vertical detachment energy) of Ag_n^- with $n \leq 4$ calculated with the additional basis functions just differ by 0.02−0.03 eV from the original ones.

To compare the results of the free Ag clusters and hydrogen binding complex clusters, the geometries and properties of the free Ag clusters in the neutral and cationic and anionic charged states have been extensively studied, and the most stable geometries were reported in our previous work.[15] On the basis of those silver cluster isomers, wherever the geometry allows it, 1-fold top, 2-fold bridge, and 3-fold face sites were tested upon the binding of hydrogen on them. For a comparison, the most stable structures for both the bare silver clusters and complex cluster structures are listed in Figure 1.

All calculations were performed with a (99, 590) pruned grid (ultrafine grid as defined in Gaussian 03). Analysis of vibrational frequencies is performed to ensure the optimized geometries as minima, not as transition structures.

Results and Discussion

Geometries of Ag_nH. When $n \leq 5$, the ground states of the neutral silver clusters have a dominantly planar structure and the metal frameworks in the most stable Ag_nH (n-N in Figure 1, where the capital letter “N” represents “neutral”) are similar to those of the ground states of the bare clusters. The previous LDA and B3LYP study[10] on the neutral silver cluster hydrides with $n \leq 5$ also shows that the silver frameworks in the bare clusters and the complexes share similar geometries. Our previous investigation shows that the most stable structure of the Ag_nCl complex does not always come from that of the lowest energy bare silver cluster plus an attached Cl atom. A similar situation is also observed in the hydrogen cases; for example, when $n = 7$, the most stable complex Ag_7H (7-N) was obtained by adding the hydrogen atom to the less stable Ag_7 isomer with C_{3v} symmetry, instead of the most stable bare cluster, which is a pentagonal pyramid with D_{5h} symmetry. It is interesting to find that H binding on other smaller Ag clusters is shared by one (top site) or two (bridge site) Ag atoms within $n \leq 6$, while it is shared by three Ag atoms (face adsorption) in Ag_7H. A similar coordination feature has also been found in the binding of H to Cu clusters. In the Cu_nH complexes ($n = 7-9$), the most preferred adsorption site is the face, while the clusters with smaller size prefer bridge or top sites.[18]

Geometries of Ag_nH^+. In all the cationic complexes on-bridge binding is preferred (Figure 1, n-C, where the capital letter “C” represents “cationic”). The structure of Ag_2H^+ has been widely studied in previous theoretical literature. In 1981, Gaspar et al.[19] studied Ag_2H^+ using a simple molecular pseudopotential method and concluded that this ion is bent. However, the calculations of Flurer and co-workers at the HF/LANL2DZ level found that the most stable structure of Ag_2H^+ is linear because of strong steric repulsions between Ag atoms.[20] More recently, Khairallah and co-workers found that Ag_2H^+ is bent using the B3LYP method.[11] In the present study, the ground state of Ag_2H^+ has a C_{2v} symmetry with a Ag−H−Ag bond angle of 109° and a Ag−H bond length of 1.74 Å. The linear

TABLE 1: NBO Atomic Charges of the H Atoms in the Lowest Energy Structures of Ag_nH, Ag_nH^-, and Ag_nH^+, $2 \leq n \leq 7$

species	charge (au)	species	charge (au)	species	charge (au)
2-N	−0.48	2-A	−0.52	2-C	−0.49
3-N	−0.36	3-A	−0.48	3-C	−0.46
4-N	−0.48	4-A	−0.44	4-C	−0.45
5-N	−0.49	5-A	−0.51	5-C	−0.41
6-N	−0.46	6-A	−0.50	6-C	−0.45
7-N	−0.52	7-A	−0.54	7-C	−0.45

Ag_2H^+ is characterized as a transition state which is only 0.11 eV less stable than the C_{2v} structure. For Ag_3H^+, our calculation characterizes a C_s structure as the most stable one in which the hydrogen atom is shared by two silver atoms, while the ^1H MAS NMR experiment has indicated that the bonding pattern is a proton shared by three equivalent Ag atoms and/or $Ag^{\delta+}$.[3] In our DFT calculations, the C_{3v} (hydrogen atom at the hollow site above the three-silver-atom plane) and D_{3h} (hydrogen atom in the middle of the Ag triangular planar) isomers of both the neutral and cationic complexes are all not local minima. Instead, the D_{3h} isomer of Ag_3H^{2+} is the global minimum. This may indicate that the silver clusters with higher charges should be considered in the experiments, but which is not the main purpose of this study. For bigger clusters, it should be noted that the most stable Ag_4H^+, Ag_5H^+, and Ag_6H^+ (4-C, 5-C, and 6-C in Figure 1) complexes, were obtained by the binding of the hydrogen atom to the framework of the less stable Ag_n^+ isomers, but not the global minima. For Ag_7H^+, notable changes in the geometry of the silver framework have been observed after the binding of hydrogen on the global minimum of Ag_7^+, which is a close-to-planar structure.

Geometries of Ag_nH^-. The low-energy structures of Ag_nH^- (n-A) are also listed in Figure 1, in which the capital letter "A" represents "anionic". The most stable complexes of Ag_nH^- are all planar or close-to-planar structures. For $n \leq 4$, the most stable anionic complexes all prefer top adsorption. For bigger clusters, $n = 5-7$, the most favorable binding site becomes the bridge site. Fischer found that, for Au_nH^- clusters ($n = 2-5$), the top sites are preferred in energy over the bridge sites.[21] The most stable structures of Ag_2H^-, Ag_3H^-, Ag_4H^-, and Ag_6H^- we obtained also have geometries very similar to those of the most stable structures Au_2H^-, Au_3H^-, Au_4H^-, and Au_6H^- they optimized.

The binding of H to silver clusters can greatly change the geometry of the silver framework, such as Ag_6H^-. The finding that the most stable structure of the complex clusters does not always come from that of the lowest energy bare silver cluster plus an attached H atom can also be observed for the anions. For Ag_4H^-, the most stable structure (4-A) is obtained by binding H to a "T"-type isomer of Ag_4^-, although the most stable structure of the bare cluster is a rhombus. The ground state of Ag_7^- is a bicapped square bipyramid with C_{3v} symmetry, while the most stable Ag_7H^- (7-A) is obtained by binding H to a silver framework close to planar.

Energetics and Bondings in the Neutral and Charged Ag_nH. Unlike gold, silver has a smaller electronegativity than hydrogen and tends to give electrons to hydrogen. Natural bond orbital (NBO) population analysis [22] shows that electrons transfer from the silver cluster to hydrogen, irrespective of the charge state. The charges on the hydrogen atoms in AgH, AgH^+, and AgH^- are −0.30, 0.03, and −0.60 au, respectively. In neutral and charged complexes Ag_nH with $2 \leq n \leq 7$, the hydrogen atom bares a certain amount of negative charge between −0.35 and −0.55 au (see Table 1). We have compared the results for the small anionic clusters AgH^-, Ag_2H^-, $HAgH^-$, and HAg_2H^- with those using larger basis sets which include three additional f-type (exponents 2.54, 0.73, and 0.20) and two additional g-type (exponents 1.58 and 0.50) functions[17] for Ag atoms. The calculated NBO charges of H in those small anionic species show differences of less than 0.02 au from the calculation results not including f and g functions for the Ag atoms. For silver hydride systems, silver acts like an alkali-metal atom and hydrogen acts like an electron acceptor. In sharp contrast, for the gold hydride systems, even in anionic gold hydrides, the hydrogen acts more like an alkali metal and contributes electrons to the valence pool of the Au_n^- clusters.[23] To reveal more details on the bonding between hydrogen and silver clusters, Table 2 tabulates the electron populations of the atomic orbitals for the complexes Ag_2H, Ag_2H^-, and Ag_2H^+. The analysis indicates that the electron flow in the neutral and charged Ag_2H is mainly from the s orbital of Ag connected to H toward to the s orbitals of H, while d orbitals have much smaller contribution and p orbitals have almost no contribution. For the other sized silver hydride clusters, a similar trend can also be observed. For the conciseness of the text, these data are reported in the Supporting Information. Different from the earlier study of the interaction between a chlorine atom and silver clusters, the d orbitals contribute more in the hydrogen−silver cluster system than in the chlorine−silver cluster system.[15] This may be due to the fact that the 1s orbital of H is higher in energy than the $3p_z$ orbital of Cl, thus resulting in a better energy match for the Ag_n 4d and H 1s orbitals.

The bindings of H to silver clusters are generally weaker than the binding of the chlorine atom. The strongest binding is found for the Ag_2H^+ cluster, which has a binding energy of 2.85 eV, while the chlorine binding energy mainly varies from 2.5 to 4.2 eV. The binding energies of the hydrogen atom as a function of cluster size for the most stable structures of Ag_nH, Ag_nH^-, and Ag_nH^+ ($n = 1-7$) (Figure 3) show an obvious odd−even oscillation. Moreover, the energies of the small anionic species Ag_n^-, Ag_nH^-, and HAg_nH^- with $n \leq 4$ were calculated by the MP2/LANL2DZ method. The adsorption energies given by MP2 are often smaller, from 0.04 to 0.51 eV, than those given by PW91PW91/LANL2DZ, but also show an even−odd oscillation. It turns out that the IP_v/VDE of the cluster can be a predictor of hydrogen−cluster bond strength. The IP_v of a neutral cluster characterizes its ability to lose an electron, while the VDE of an anion cluster characterizes its ability to lose an electron. It is easier for clusters with an odd number of electrons (with lower IP_v for neutrals or lower VDE for anions) to donate an electron than the clusters with an even number of electrons (with higher IP_v for neutrals or higher VDE for anions). As a result, the clusters with an odd number of electrons bind H more strongly than their neighbor clusters with an even number of electrons. The oscillation of the binding energy related to the IPs/VDEs of the pure metal clusters has also been extensively reported in other literature.[17,24] It should be noticed that in those studies the adsorbates are all electron acceptors when binding to clusters, while, recently, studies show that if the adsorbate binds to clusters by donating electrons, there is a good correlation between the binding energy of the adsorbate and the energy of the LUMO of the clusters.[25]

Two additional trends can be observed in the binding energies: (a) The differences in binding energies for the different charge states become increasingly smaller. This can be simply understood on the basis that as the cluster size increases the same charge (the charge of the excess electron) is distributed within a larger volume so that the excess charge density becomes

TABLE 2: NBO Population Analysis for Ag_2, Ag_2^-, Ag_2^+, Ag_2H, Ag_2H^-, and Ag_2H^+

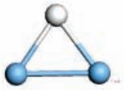
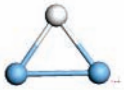
H				H	
	charges			0	
	s			1.00	
	p				
	d				
Species		Ag_1	Ag_2	H	
Ag_2	charges	0.00	0.00		
	s	3.01	3.01		
	p	6.01	6.01		
	d	9.98	9.98		
Ag_2H	charges	+0.242	+0.242	-0.483	
	s	2.81	2.81	1.48	
	p	6.01	6.01		
	d	9.94	9.94		
Ag_2^-	charges	-0.500	-0.500		
	s	3.50	3.50		
	p	6.02	6.02		
	d	9.98	9.98		
Ag_2H^-	charges	+0.153	-0.638	-0.515	
	s	2.91	3.66	1.51	
	p	6.02	6.01		
	d	9.92	9.97		
Ag_2^+	charges	+0.500	+0.500		
	s	2.50	2.50		
	p	6.02	6.02		
	d	9.98	9.98		
Ag_2H^+	charges	+0.745	+0.745	-0.490	
	s	2.31	2.31	1.49	
	p	6.01	6.01		
	d	9.94	9.94		

TABLE 3: Vibrational Frequencies (cm^{-1}) Involving Both Ag and H for Ag_nH, Ag_nH^-, and Ag_nH^+, $2 \leq n \leq 7$

species	frequencies	species	frequencies	species	frequencies
2-N	685, 1450	2-A	280, 1487	2-C	1120, 1276
3-N	182.238, 1643	3-A	236, 280, 1536	3-C	137, 1055, 1314
4-N	326,835, 1115	4-A	234, 273, 1553	4-C	179, 1006, 1375
5-N	347,938, 1118	5-A	353, 919, 1078	5-C	265, 1053, 1141
6-N	277, 921, 1120	6-A	335, 1052, 1108	6-C	303, 996, 1116
7-N	525, 529, 909	7-A	357, 788, 1034	7-C	276, 987, 1134

smaller. (b) For cationic clusters there is an evident gradual decrease of the magnitude of the oscillation as the cluster size increases, whereas no obvious change in magnitude can be seen for the neutrals and anions. Clearly, multiple factors, such as the electrostatic interactions and the strength of the orbital interactions, all contribute to the quantitative value of the binding strength. It is difficult to explain these subtle differences in a uniform way with just one special factor.

Frequency calculation results may help the experiments to determine how the hydrogen binds to the Ag atoms. The vibrational frequencies involving both Ag and H are listed in Table 3. The experimental Ag−H bond length of AgH is 1.618 Å and its vibrational frequency is 1717.0 cm^{-1},[9] in good agreement with our PW91PW91 results, 1.611 Å and 1738 cm^{-1}. For the anionic and cationic monohydrides, we characterized the Ag−H stretching frequency as 1318 and 1182 cm^{-1}, respectively, indicating a weaker bond between ionic Ag and H than that between a Ag atom and H. In the bigger complex clusters, Ag−H frequencies vary according to the way the Ag atoms bonded to the hydrogen. The largest Ag−H frequencies calculated generally increase in the order face < bridge < top adsorption. For top-site adsorption, such as in the neutral Ag_3H and anionic Ag_2H^-, Ag_3H^-, and Ag_4H^-, the largest Ag−H stretching frequencies are more than 1487 cm^{-1}. On the other hand, in the only face adsorption complex, Ag_7H, the Ag−H stretching frequency is no more than 1000 cm^{-1}. For most bridge adsorption complexes (except Ag_2H), the largest Ag−H stretching frequencies fall in the range of 1034 cm^{-1} (Ag_7H^-) to 1375 cm^{-1} (Ag_4H^+).

Table 4 shows the lowest dissociation energies at 0 K for the neutral and charged Ag_nH complexes. The results indicate that, irrespective of the charge state, the most favorable channel at 0 K is the evaporation of a Ag atom or a AgH molecule, corresponding to the processes in which the larger fragment should be close-shelled. In some cases the ejections of Ag_2 and AgH are the two competing dissociation channels. For Ag_4H,

TABLE 4: Energetically Preferred Dissociation Channels of Ag_nH, Ag_nH^-, and Ag_nH^+, $2 \leq n \leq 7$, at 0 K

neutrals	*E* (eV)	anions	*E* (eV)	cations	*E* (eV)
$Ag_2H \rightarrow AgH + Ag$	0.79	$Ag_2H^- \rightarrow Ag^- + AgH$	1.95	$Ag_2H^+ \rightarrow Ag^+ + AgH$	2.34
$Ag_3H \rightarrow Ag_2 + AgH$	0.92	$Ag_3H^- \rightarrow Ag_2H^- + Ag$	1.36	$Ag_3H^+ \rightarrow Ag_2H^+ + Ag$	1.11
$Ag_4H \rightarrow Ag_3H + Ag$	1.56	$Ag_4H^- \rightarrow Ag_3^- + AgH$	1.52	$Ag_4H^+ \rightarrow Ag_3^+ + AgH$	1.45
$Ag_5H \rightarrow Ag_4 + AgH$	2.07	$Ag_5H^- \rightarrow Ag_4H^- + Ag$	1.46	$Ag_5H^+ \rightarrow Ag_4H^+ + Ag$	1.28
$Ag_6H \rightarrow Ag_5H + Ag$	1.22	$Ag_6H^- \rightarrow Ag_5^- + AgH$	1.75	$Ag_6H^+ \rightarrow Ag_5^+ + AgH$	1.74
$Ag_7H \rightarrow Ag_6 + AgH$	1.49	$Ag_7H^- \rightarrow Ag_6H^- + Ag$	1.53	$Ag_7H^+ \rightarrow Ag_6H^+ + Ag$	1.67

Ag_7H, Ag_4H^-, and Ag_6H^-, the energy differences between ejecting a AgH molecule and ejecting a Ag_2 molecule are less than 0.10 eV. An odd−even behavior in the dissociation energies is observed, for both anions and cations. For the neutrals, the trend of the oscillation fails between $n = 2$ and $n = 3$. The general odd−even alternation can be explained by the high stability of clusters with an even number of valence electrons.

Geometries and Energetics of HAg_nH^-. On the basis of the optimized anionic geometries (*n*-A in Figure 1), we optimized the geometries of HAg_nH^- (two H atoms binding on Ag_n^-) and calculated the secondary binding energies by $E_b = E(Ag_nH^-) + E(H) - E(HAg_nH^-)$. Here $E(HAg_nH^-)$ is the energy of the structures of HAg_nH^- listed in Figure 2. The binding of the second H to Ag_nH^- has a binding energy in the range from 1.67 eV (HAg_2H^-) to 2.98 eV ($HAgH^-$), almost as strong as the first H binding. The binding energies of the second H also show an odd−even oscillation as a function of the cluster sizes. HAg_nH^- clusters with even *n* have a larger binding energy than HAg_nH^- clusters with odd *n*. The optimized lowest energy structures are those with two H atoms shared with only one Ag atom and still remain planar or close-to-planar (see Figure 2).

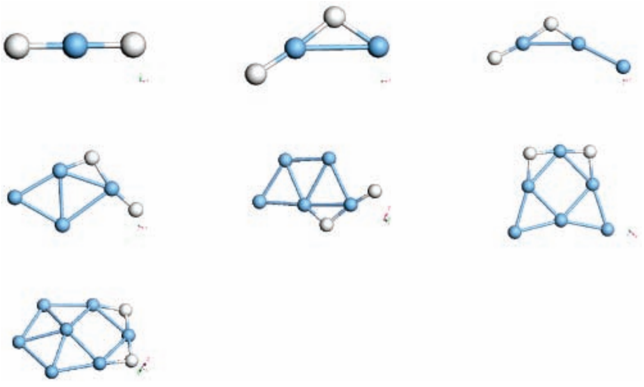


Figure 2. Optimized geometries of the most stable HAg_nH^-, $1 \leq n \leq 7$.

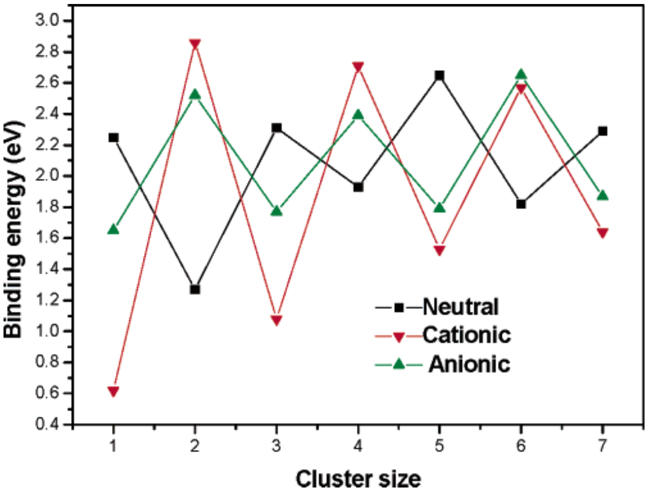


Figure 3. Binding energies (eV) vs cluster size of Ag_nH, Ag_nH^-, and Ag_nH^+, $1 \leq n \leq 7$.

The framework of the silver parts is subjected to considerable structural change in HAg_nH^- as compared to Ag_nH^- when $n =$ 6 and 7. Each of the hydrogen atoms in the HAg_nH^- complexes bares a negative charge of about −0.50 au, leaving almost no charge on the framework. It was found that the framework of the silver parts in most HAg_nH^- clusters are very similar to the most stable structure of neutral Ag_n with $n = 2-6$.

Conclusions

In this work, we have systematically studied the interaction of the hydrogen atom with small neutral and charged silver clusters in the size range of one to seven silver atoms. It was found that the most stable structure of the Ag_nH complex (neutral or charged) does not always come from that of the lowest energy bare silver cluster plus an attached H atom and the binding of H can greatly change the geometries of the bare silver clusters in some cases, such as Ag_6^-. The calculation results indicate that bridge sites are the most favorable binding sites for the cationic and most of the neutral clusters. For anions, top sites are preferred in smaller clusters within $n = 4$, while bridge sites are preferred in bigger clusters. For the HAg_nH^- clusters, the lowest energy ones are planar or close-to-planar structures in which the two H atoms reside on two sides of the same Ag atom. The calculated binding energies show remarkable odd−even alternation behaviors. Population analysis indicates that silver acts like an alkali-metal atom in the interaction between H and silver clusters.

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Supporting Information Available: Tables of net atomic charges of the adsorbates, zero-point vibrational energies (ZPEs), electronic energies (E_e), and $\langle S^2 \rangle$ for the neutral and charged Ag_nH ($n = 2-7$) clusters.

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