THEORETICAL INVESTIGATIONS OF SILVER CLUSTERS AND SILVER-LIGAND SYSTEMS

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1. Introduction

Studies directed at understanding structural and electronic properties of silver clusters have been and remain the subject of an active theoretical [1-22] and experimental [23-38] effort. One of the reasons is the (still) important role these systems play in the photographic process. Investigations of interactions of silver clusters with different atoms and molecules are motivated primarily by a possible utility of these clusters in catalytic processes. The important role of silver in the selective oxidation of ethylene into ethylene oxide, the feedstock for polyester production, is well-known [39]. Possible variations in chemical reactivity with the cluster size and understanding of the mechanisms of interactions with different ligands may lead to new and more efficient applications. Investigations of cluster-ligand systems also contribute a great deal to a better understanding of gas-surface interactions. Accordingly, theoretical studies of silver clusters and cluster-ligand systems [40-44] fall into two categories - those that use clusters as models for silver surfaces [40], and those that target clusters and cluster-ligand interactions as subjects in their own right [41-44]. The common goal of all these studies is to elucidate the nature of the interatomic interactions and bonding at the microscopic level and thereby arrive at a fundamental understanding and description of the various structural and electronic properties.

Most experimental investigations of silver cluster-ligand systems utilize spectroscopic techniques [45-51]. These were applied to examine the potential energy surface and disassociation dynamics of $\text{Ag}_2\text{-NH}_3$ [47], the interaction of Ag_n with $(\text{C}_6\text{H}_6)_m$, $n=3-7$, $m=1-4$ [48], and details of the structure and bonding of the Ag_nC_{60} , $n=1-4$, complex [49]. Two recent studies use a combination of infrared photodissociation and photoionization spectroscopies to examine the effects of complexation of Ag_n , $n=3-7$, clusters with C_2H_4 and $\text{C}_2\text{H}_4\text{O}$ molecules [50] and Ag_n , $n=3-22$, with CH_3OH [51].

The ground (^2S) state of the Ag atom with a $[\text{Kr}]4d^{10}5s^1$ electronic configuration is well-separated ($\Delta E = 3.75$ eV [52]) from the first excited (^2D) state with a $[\text{Kr}]4d^95s^2$ configuration. The d orbitals, including the 4d ones, are much more localized than the 5s orbital(s) (the average orbital radius $\langle r \rangle_{4d} = 0.72$ Å, whereas $\langle r \rangle_{5s} = 1.94$ Å [52]). Bonding in silver clusters is dominated by the 5s electrons, which suggests that they may, at least in some respects, be similar to those of alkali metal clusters. In a number

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of theoretical studies of pure silver clusters the atoms were treated as effectively one-electron systems [1,2,13,16]. The influence of the 46 inner ("core") electrons was represented by an effective core potential (ECP). Structural and energy characteristics were computed within the Hartree-Fock (HF) and configuration interaction (CI) frameworks. CI treatments with ECPs corresponding to smaller cores, a 36-electron (11 valence electrons) [5,6,9,11,12] and a 28-electron (19 valence electrons) [3,4,7,8], have also been performed. These, however, are very computationally demanding and only small sized symmetric clusters ($n=2-6$) of silver were studied and often the structures of these clusters were obtained using highly constrained minimization. An additional problem in these studies is that despite their greater rigor, the binding energies and ionization potentials are systematically underestimated in CI calculations for silver clusters.

An operationally more efficient way of including electron correlation effects is to use the density functional theory (DFT). DFT studies of silver clusters were performed within the local spin density (LSD) approach [1,2] and using non-local generalized gradient approximations (GGA) [14,15,20]. Different exchange-correlation functionals were utilized, and the computations were carried out not only with ECPs [1,2,20] but also considering all the electrons explicitly [14,15]. A recent treatment [20] is based on a distance dependent tight-binding Hamiltonian, of the type used earlier for alkali metal clusters, with parameters fitted to data obtained through DFT computations.

Theoretical investigations of silver-ligand complexes include interactions of Ag atoms and small Ag_n , $n \leq 4$, clusters with H, Cl, O, O_2 , OH [40], C_2H_4 [40,41], H_2O , CO [41], NH_3 [41,47], $(\text{C}_6\text{H}_5)_4$ [42], and C_6H_6 [43,44]. In Ref. 40, the Ag_3 cluster is treated within the generalized valence bond (GVB) approach and is used to study chemisorption of ligands on (110) and (111) surfaces of silver. $\text{Ag}_2\text{-L}$, $\text{L} = \text{C}_2\text{H}_4$, H_2O , CO, NH_3 , complexes were treated at HF and post-HF levels using modified coupled pair functional (MCPF) and second-order Møller-Plesset (MP2) corrections [41]. The interaction of a silver atom with a benzene molecule was treated within a complete active space self-consistent field (CASSCF) approach [43]. DFT computations were performed to study interactions of Ag_2 with NH_3 [47] and Ag_4 with $(\text{C}_6\text{H}_5)_4$ [42]. The subjects of these investigations are geometric characteristics and bond strengths of the cluster-ligand complexes. Unconstrained geometry optimizations give silver-ligand distances that range from 2.19 Å in the $\text{Ag}_2\text{-NH}_3$ system [47] to 2.72 Å in the $\text{Ag}_2\text{-C}_2\text{H}_4$ complex. The bond strengths vary from 0.53 eV in $\text{Ag}_2\text{-NH}_3$ [47] (the experimental value is 0.64 eV) to 0.42 eV in $\text{Ag}_2\text{-C}_2\text{H}_4$ [41].

Notwithstanding the past efforts and progress, silver clusters and silver-ligand systems remain a subject of continued interest and active research. One of the reasons for this is that the quantitative, and at times even the qualitative, characteristics arrived at within different approaches, all of which involve approximations, do not necessarily agree. Since the implications, especially the quantitative ones, of the approximations involved are often unknown or are difficult to assess, the robustness of the different findings can be evaluated only through carrying out complementary studies. Those, which can be expected to be of higher accuracy - and which are, as a rule, computationally more demanding - are especially important and should be performed as the progress in computational capabilities makes them feasible. Another goal of the current theoretical studies is extensions to clusters of larger sizes and new cluster-ligand systems.

Motivated by the mentioned considerations, we performed a series of DFT-based investigations of bare Ag_n , $n \leq 8$, clusters and of a variety of silver-ligand systems. The latter include the $\text{Ag}_3\text{C}_2\text{H}_4$ complex and stoichiometric $(\text{AgX})_n$, $\text{X}=\text{Cl}, \text{Br}$, $n=1-4$, clusters. Globally and locally stable geometric structures (isomers) of the clusters and cluster-ligand complexes are obtained for the neutral and charged states of the species. The properties computed include electronic characteristics such as binding energy (BE), vertical and adiabatic ionization potential (IP_v and IP_a), vertical (electron) detachment energy (VDE), and adiabatic electron affinity (EA). Charge distributions in the systems are obtained using the Mulliken population analysis and are utilized to characterize the nature of bonding.

Our study of the $\text{Ag}_3\text{C}_2\text{H}_4$ system is motivated by recent infrared photoionization experiments on $\text{Ag}_n(\text{C}_2\text{H}_4)_m$ complexes [50], which indicate that the IP_v s of the complexes are systematically lower than those of the corresponding bare Ag_n clusters. One of the interesting findings of our study is that the change in the IP_v caused by the association of Ag_3 with C_2H_4 can serve as indicator of the structure of the $\text{Ag}_3\text{C}_2\text{H}_4$ complex. Small silver-halide systems are the subject of only a limited number of investigations. The only experimental work we are aware of is mass-spectrometric measurements of the abundance of Ag_nBr_m clusters in the size range $2 \leq n \leq 14$, $m \leq n$ [53]. Earlier theoretical studies aimed at bulk and surface properties of silver-halides, which are of relevance in photographic processes, and therefore the clusters considered were either frozen in bulk-like structures or optimized to mimic surface reconstruction and/or the effect of impurities [54-56]. In contrast, the focus of our studies is on geometric and electronic properties of small stoichiometric silver-halide clusters per se.

The paper is organized as follows. The methodology and the computational details are presented in the next section. The results are described and discussed in section 3, which is subdivided into three subsections devoted, respectively, to bare silver clusters, the $\text{Ag}_3\text{C}_2\text{H}_4$ complex, and the silver-halide systems. A summary is given in section 4.

2. Methodology and Computational Details

Our investigations are carried out within the DFT framework using non-local exchange-correlation functionals as implemented in the Gaussian-94 package [57]. In general, the results may and do depend on the particular choice of the functional and the details of the description of the electrons. One may partition the electrons of an atom into the "inner" (core) ones, which together with the nucleus are then represented by an ECP, and the "outer" (valence) ones, the wave function of which is expanded in terms of a chosen basis set. Alternatively, one may opt for an "all-electron treatment", i.e., consider all the electrons explicitly. The results are, in general, also affected by the choice of the ECP and of the basis set. In the absence of general guidelines as to the best, or at least optimal, selection of the exchange-correlation functional (the number of these continues to grow), ECP, and/or basis set, one would have to explore all the possible combinations. This approach, however, would not only be inefficient (or even impractical), but also could be not very meaningful since the choice of an ECP and of a basis set should be inherently consistent. Apart from the general issue of the transferability of ECPs, use, for example, of a HF-based ECP in DFT computations is

a ground for additional concern [58]. As a rule, for transition and noble metals, the larger the size of an ECP the lower the degree of its transferability [59].

The functionals utilized in computations on bare silver clusters and the $\text{Ag}_3\text{C}_2\text{H}_4$ system are those of Becke [60] for the exchange part and of Perdew-Wang [61] for the correlation contribution (BPW91). Becke's 3-parameter exchange functional [62] coupled with Lee-Yang-Parr's correlation functional [63,64] (B3LYP) is used to treat the silver-halide systems. For Ag_n clusters and $\text{Ag}_3\text{-C}_2\text{H}_4$ system, a 28-electron core ($[\text{Ar}]3d^{10}$) of each silver atom is represented by a HF-based semi-relativistic effective core potential [65] (to be referred to as ECP1), which is used in conjunction with a contracted Gaussian basis set of the form (311111/22111/3111) for expansion of the wave function of the remaining 19 valence electrons. For $(\text{AgCl})_n$ and $(\text{AgBr})_n$ clusters an alternate 28-electron core semi-relativistic ECP [66] (ECP2) is used on silver atoms accompanied by contracted Gaussian basis set of the form (441/321/31) for the valence electrons. Relativistic effects can be expected to be significant for large atoms such as silver and calculations employing semi-relativistic ECPs partially include these effects.

The specific functionals and ECPs and/or basis sets were chosen after considering results for the structures and electronic characteristics for Ag, Ag_2 and Ag_3 using the two 28-electron core ECPs [65,66] and basis sets mentioned, as well as an all-electron DFT-based set of (633321/53211/531) contracted Gaussians [67] combined with different functionals. The results of the test calculations using BPW91, B3LYP and BP86 (Becke exchange [60] combined with Perdew correlation [68]) and different ECPs/basis sets are presented in Tables 1a, 1b and 1c together with experimental data. Inspection of the table shows that the results obtained using the 28-electron-core ECPs are comparable to those following from the all-electron treatment, with the particular combination of BPW91 used with ECP1 (and accompanying basis set) and B3LYP used with ECP2 giving the best results.

TABLE 1a. Comparison of computed values of IP and EA of Ag atom obtained using different combinations of basis sets and functionals.

Approach		IP (eV)	EA (eV)
AHDSP-ECP [§]	BPW91	7.99	1.31
	B3LYP	7.95	1.38
	BP86	8.18	1.54
HW-ECP [‡]	BPW91	6.83	1.44
	B3LYP	6.90	1.53
	BP86	7.00	1.68
All-electron [†]	BPW91	7.38	1.00
	B3LYP	7.37	0.92
	BP86	7.55	1.15
Experiment		7.576	1.30

[§] Ref. [65], [‡] Ref. [66], [†] Ref. [67]

TABLE 1b. Comparison of results for the bond lengths and binding energies for the silver dimer, using two different 28-electron core ECPs and an all-electron basis, combined with different functionals.

Approach		r (Å)	ω (cm ⁻¹)	BE/n (eV)
AHDSP-ECP [§]	BPW91	2.58	179.7	0.80
	B3LYP	2.60	174.1	0.75
	BP86	2.57	182.8	0.86
HW-ECP [‡]	BPW91	2.60	169.5	0.87
	B3LYP	2.62	163.6	0.86
	BP86	2.59	172.9	0.94
All-electron [†]	BPW91	2.68	151.7	1.01
	B3LYP	2.70	151.6	0.92
	BP86	2.67	153.2	1.10
Experiment		2.48% 2.53 [#]	192.4%	0.83%

[§] Ref. [65], [‡] Ref. [66], [†] Ref. [67], ^{*} Ref. [24], [#] Ref. [28]

TABLE 1c. Comparison of results for the geometries and binding energies for the silver trimer, using two different 28-electron core ECPs and an all-electron basis, combined with different functionals.

Approach		r (Å)	θ°	BE/n (eV)
AHDSP-ECP [§]	BPW91	2.63	70.6	0.78
	B3LYP	2.67	141.1	0.72
	BP86	2.63	70.6	0.84
HW-ECP [‡]	BPW91	2.65	69.6	1.03
	B3LYP	2.68	74.1	0.96
	BP86	2.64	69.2	1.11
All-electron [†]	BPW91	2.75	74.5	0.99
	B3LYP	2.77	113.2	0.88
	BP86	2.74	73.9	1.09
Experiment		-	-	0.87%

[§] Ref. [65], [‡] Ref. [66], [†] Ref. [67], ^{*} Ref. [23]

As could be expected, there are variations in these results, which depend not only on whether or not the calculation uses an ECP but also on the choice of the specific functionals used within the DFT framework. A noticeable trend in these results is the consistently longer bond distances obtained in all the DFT approaches with the all-electron basis, as compared with those obtained using semi-relativistic ECPs. All-

electron Gaussian basis functions are used for all the other atoms – Dunning double zeta [69] with a polarization function - (6111/41/1) basis for C, (31/1) basis for H (to describe ethylene), (531111/421/1) basis for Cl and (63311/5311/411) basis for Br.

Extensive searches performed for stable (globally or locally) structural forms for all the systems (Ag_n clusters, $\text{Ag}_3\text{-C}_2\text{H}_4$, $(\text{AgCl})_n$ and $(\text{AgBr})_n$) resulted in the isomers described in this paper. While the searches were exhaustive, there is no guarantee that all the equilibrium structures of these systems were found. The optimizations used are standard gradient-based [70] techniques. Both symmetric and asymmetric initial configurations were used as inputs in the search procedure and complete optimization (no symmetry constraints imposed) of all degrees of freedom was performed. A normal mode analysis was carried out for each of the resulting stationary configurations to separate the true equilibrium structures from those representing saddle-points on the corresponding potential energy surfaces. Results for the stable structural forms of the clusters and cluster-ligand systems are given in the next section. The properties investigated are the geometries and binding energies (BE) of the clusters and complexes, their vertical and adiabatic ionization potentials (IP_v and IP_a), and for the case of pure silver clusters, the vertical (electron) detachment energy (VDE) and adiabatic electron affinity (EA_a) as well. The binding energy of the isomers of the clusters are calculated as

$$\begin{aligned}\text{BE} [\text{Ag}_n] &= n\text{E}[\text{Ag}] - \text{E}[\text{Ag}_n], \\ \text{BE} [\text{Ag}_n^+] &= (n-1) \text{E}[\text{Ag}] + \text{E} [\text{Ag}^+] - \text{E}[\text{Ag}_n^+], \\ \text{BE} [\text{Ag}_n^-] &= (n-1) \text{E}[\text{Ag}] + \text{E} [\text{Ag}^-] - \text{E}[\text{Ag}_n^-],\end{aligned}\tag{1}$$

where $n\text{E}[\text{Ag}]$ is the energy of n non-interacting Ag atoms, and $\text{E}[\text{Ag}_n]$ the total energy of the Ag_n cluster in the equilibrium configuration of the isomer under consideration. The computation of the binding energies of isomers of Ag_n ions follows a similar analogy. Alternatively, the binding energies of the cationic and anionic clusters can be calculated in terms of the adiabatic ionization potentials and electron affinities, as

$$\begin{aligned}\text{BE} [\text{Ag}_n^+] &= \text{IP}[\text{Ag}] - \text{IP}_a[\text{Ag}_n] + \text{BE}[\text{Ag}_n], \\ \text{BE} [\text{Ag}_n^-] &= \text{BE}[\text{Ag}_n] + \text{EA}_a[\text{Ag}_n] - \text{EA}[\text{Ag}];\end{aligned}\tag{2}$$

where E denotes the equilibrium total energy, IP - the atomic ionization potential, EA - the atomic electron affinity. The IP s are calculated as the difference between the energies of the ground (electronic) states of the appropriate neutral and cationic species. The difference between the energies of the neutral and anionic species, both fixed in the equilibrium structure of the negatively charged cluster, gives the VDEs of the cluster. The EA_a s are computed as a difference between the equilibrium energies of the ground states of the neutral and the anionic species. The binding energy of the silver-molecule complex is calculated with respect to the binding energies of the constituent entities (silver trimer and ethylene) as

$$\text{BE} [\text{Ag}_3\text{C}_2\text{H}_4] = \text{E}[\text{Ag}_3] + \text{E} [\text{C}_2\text{H}_4] - \text{E}[\text{Ag}_3\text{C}_2\text{H}_4]\tag{3}$$

where E denotes the equilibrium total energy of the species within the brackets. In case of the silver-halide clusters, the following expression is used to obtain the binding energy per AgX pair:

$$BE [(AgX)_n] \text{ (per AgX pair)} = \{nE[Ag] + nE[X] - E[(AgX)_n]\}/n, \quad X = Cl \text{ or Br. (4)}$$

3. Results and Discussion

3.1 BARE SILVER CLUSTERS

The lowest energy isomers of the neutral, cationic and anionic Ag_n clusters obtained in our calculations are shown in Figs. 1, 2 and 3 respectively.

3.1.1 Ag_2 , Ag_2^+ , Ag_2^-

The dimer and trimer are the most extensively studied silver clusters, theoretically as well as experimentally. Our investigations on the ground state ($^1\Sigma_g$) of the dimer give a binding energy of 1.60 eV (0.80 eV/atom) and a bond length of 2.58 Å. The experimentally [24] measured values for the binding energy and bond length of Ag_2 are 1.65 ± 0.03 eV and 2.48 Å, respectively. A second study [28] using laser induced fluorescence to examine the rotational states of Ag_2 infers a bond length of 2.53 Å.

The cation Ag_2^+ has an equilibrium bond distance of 2.75 Å and a binding energy of 1.68 eV, comparable to that of the neutral dimer. These results support the conclusions of photoelectron spectroscopic experiments [27] that the binding energies of Ag_2 and Ag_2^+ have very similar values. The calculated vertical and adiabatic ionization potentials (IP_v and IP_a) for the dimer are 7.98 eV and 7.92 eV respectively. The experimental value of the vertical IP for the dimer is 7.56 eV [24]. Calculations reveal that the anion Ag_2^- , with a binding energy of 1.40 eV and a bond length of 2.71 Å is less bound than either Ag_2 or Ag_2^+ . The experimental value for the binding energy of Ag_2^- is 1.37 ± 0.16 eV [27]. Both ions have longer bond lengths than the neutral Ag_2 cluster. The calculated vertical detachment energy of 1.15 eV is in reasonable agreement with the experimental value of 1.06 ± 0.02 eV [27]. The calculated adiabatic electron affinity for the dimer is 1.09 eV.

3.1.2 Ag_3 , Ag_3^+ , Ag_3^-

Ag_3 is a Jahn-Teller distorted cluster. The stable ground state equilibrium geometry for the neutral Ag_3 trimer is an isosceles triangle of C_{2v} symmetry with sides of length 2.63 Å, and apex angle 70.6°. The calculated binding energy for Ag_3 is 2.33 eV, as compared with the experimental result [23] of 2.60 eV. Our results for the neutral trimer agree with the majority of other studies [1-6,10,13,20], which find that the global minimum for Ag_3 is an "obtuse" (in this context having an apex angle larger than 60°) isosceles triangle. However, there are differences between the optimal structures obtained using various approaches owing to the flatness of the potential energy surface of Ag_3 and the consequent difficulty in accurately locating the minimum. Investigations using the Becke 3-parameter exchange combined with Lee, Yang and Parr correlation functional (B3LYP) and the ECP1+(311111/22111/3111) basis [65], result in a "bent" (with an apex angle of 141.1°) structure for Ag_3 (see table 1c). A bent structure (apex angle of 113.2°) is also obtained when B3LYP is used in conjunction with the all-electron basis set [67].

Figure 1. The lowest energy isomers for Ag_n clusters ($2 \leq n \leq 8$).

Figure 2. The lowest energy isomers for Ag_n^+ clusters ($2 \leq n \leq 8$).

Silver trimer shows interesting structural changes upon ionization. The cation Ag_3^+ in the singlet ground state, is an equilateral triangle with sides of length 2.70 Å, while the anion Ag_3^- in the $S=0$ state has a linear geometry with bond lengths of 2.66 Å. Both ions, Ag_3^+ and Ag_3^- , are more strongly bound than the neutral cluster, with binding energies of 4.40 eV and 3.39 eV respectively, and indicate a definite preference for a closed shell structure. For Ag_3^+ , a Mulliken charge analysis reveals that the excess positive charge is distributed equally over all the constituent Ag atoms for the

Figure 3. The lowest energy isomers for Ag_n^- clusters ($2 \leq n \leq 8$).

equilateral triangle geometry of the cation, consistent with this conformation. A similar charge analysis for Ag_3^- indicates that the excess negative charge is localized on the two end atoms of the linear chain, equally consistent with the fact that repulsion of the like charges is minimized in a conformation that maximizes the distance between the two end atoms. The calculated vertical ionization potential for Ag_3 is 6.08 eV, and the adiabatic IP (corresponding to a rearrangement of atoms to an equilateral triangle in the cation) is 0.16 eV lower at 5.92 eV. Experimental measurements of the vertical IP for the silver trimer give 5.6 eV [30] and 6.0 eV (upper bound [29]), significantly smaller than that of the dimer. We obtain a vertical detachment energy (VDE) of 2.37 eV for the ground state linear structure of the silver trimer comparable to the experimental

value of 2.43 ± 0.01 eV [27]. Our calculated adiabatic electron affinity is 2.36 eV as compared with the experimental estimate of 2.32 eV [27].

3.1.3 Ag_4 , Ag_4^+ , Ag_4^-

The ground state equilibrium structure for the neutral silver tetramer is a rhombus with sides of length 2.75 Å, and a shorter diagonal distance of 2.62 Å. The calculated binding energy is 4.16 eV for this isomer. There is a general agreement between all the theoretical studies [1,6,9,11,13,15,20] on the neutral silver tetramer, that the rhombus is the ground state equilibrium structure.

The lowest energy isomer of the positive ion is also a rhombus and with a binding energy of 5.52 eV, is substantially more bound than the neutral species. The calculated vertical ionization potential for the rhombus structure of Ag_4 is 6.65 eV, which coincides with the measured [29] upper bound on the IP_v of 6.65 eV for Ag_4 . The adiabatic ionization potential is not very different at 6.64 eV and is consistent with the fact that there is little change in structure upon ionization of the neutral rhombus to the rhombus structure of the cation.

Although our aim is to present only the lowest energy isomers of neutral, cationic and anionic silver clusters in this paper it is worthwhile to make an exception for cases where two (or more) isomers are very close in energy, as in the case of Ag_4^- . We find two (energetically) close-lying isomers for the negatively charged tetramer - the rhombus and a linear chain structure. The linear structure is 0.0004 eV higher in energy than the rhombus, and is degenerate for all practical considerations. The binding energies of these two isomers are 4.56 eV. The third isomer of Ag_4^- is a Y-shaped structure with a C_{2v} symmetry, and with a binding energy of 4.51 eV is only 0.05 eV higher in energy than the two lower energy structures. This close proximity in energy of all three isomers of Ag_4^- has also been noted in previous all-electron DFT calculations [14] on Ag_4^- . In contrast, the HF/CI investigations [16] on this system find an energy difference of 0.45 eV between the rhombus and the linear chain at the HF level and $\Delta E = 0.57$ eV for the CI energy calculation on the HF optimized geometries. The larger binding energy for the ionic species (as compared with the neutral) in the case of the silver trimer and tetramer has also been seen in previous studies [1,6,13] on silver clusters. The calculated vertical detachment energy (VDE) for the rhombus is 1.79 eV, approximately 10% higher than the experimental result of 1.65 ± 0.05 eV [27], while the calculated adiabatic electron affinity is 1.71 eV. All the equilibrium structures obtained for the tetramer (neutral, anion and cation) are planar geometries.

3.1.4 Ag_5 , Ag_5^+ , Ag_5^-

The lowest energy geometry of the neutral Ag_5 cluster is a planar W-shape structure, similar to that found for Li_5 , Na_5 and Cu_5 . While there are small differences in the bond distances, there is a general agreement between our results and previous theoretical investigations [9,13,15,20]. Recent Raman spectra experiments [38] on Ag_5 clusters isolated in solid argon matrix find, by comparing their data to theoretical frequency calculations on this system, that the structure most consistent with the analysis of the observed frequencies and their intensities is the planar trapezoidal (W-shape) form of Ag_5 . The binding energy for this isomer is 5.71 eV. While the lowest energy geometry associated with the ground state is still planar for the neutral Ag_n cluster at $n=5$, 3-dimensional isomers do begin to emerge at $n=5$, as higher energy isomers for the neutral pentamer, and as the lowest energy isomer for the cation.

The lowest energy structure of the cation in the singlet spin state is a 3-dimensional one, made up of two non-planar triangular units in a D_{2d} symmetry. This structure has a binding energy of 7.63 eV. The calculated vertical IP for Ag_5^+ is 6.32 eV - experimental results are 5.75 eV [30] and 6.35 eV (upper bound, [29]). The calculated adiabatic IP is 6.08 eV.

The ground state of the anion has a planar W-shaped structure, with a binding energy of 6.48 eV. The calculated vertical detachment energy for the lowest energy geometry is 2.10 eV, while the experimental value [27] for Ag_5^- is 2.11 ± 0.05 eV. The calculated adiabatic electron affinity is 2.08 eV.

3.1.5 Ag_6 , Ag_6^+ , Ag_6^-

There is considerable disagreement in literature about the ground state geometry of neutral Ag_6 . Four independent theoretical studies have been carried out previously on Ag_6 . The first study, using CI calculations with a 36-electron core ECP [12] and a five-fold symmetry imposed on the Ag_6 structure, finds that the lowest energy isomer of the hexamer is a pentagonal pyramid. A second investigation [13] uses an optimization at the Hartree-Fock level with a 46-electron core (1-valence electron) ECP and finds two isomers very close in energy. One isomer is a pentagonal pyramid with the apex Ag atom located very close to the plane of the pentagon and the other is a tetrahedral C_{2v} structure, only 0.06 eV higher in energy. The frequency analysis for these structures was not considered very reliable for the flat potential energy surfaces that resulted. The third study, a DFT calculation [15] with an all-electron basis, finds the lowest energy geometry of Ag_6 to be a planar trigonal structure, 0.15 eV lower in energy than the pentagonal pyramid. A recent calculation [20] using a tight-binding Hamiltonian to describe Ag_6 also finds the planar structure as the lowest energy one, the other two isomers found in this work are 0.18 eV higher in energy. Our results are similar to the last two studies - we find that the lowest energy isomer is a planar trigonal one with a binding energy of 7.86 eV. The pentagonal pyramid is 0.28 eV higher in energy than the planar structure, indicating that the lowest energy isomer of neutral silver cluster still has a planar geometry at $n=6$. In terms of the different calculations on the lowest isomer of Ag_6 , all the Hartree-Fock and HF-based calculations predict that the lowest energy isomer structure of the neutral hexamer is 3-dimensional, while all the DFT and DFT-based calculations predict a planar lowest energy structure.

The lowest energy geometry of the Ag_6^+ cation is a tripyramid with C_{2v} symmetry. The binding energy of the cation is significantly larger than that of the neutral species, at 8.90 eV. The calculated vertical IP of Ag_6^+ is 7.19 eV and the computed adiabatic IP is 6.68 eV, as compared with the experimental upper bound of 7.15 eV [29] on the IP_v of Ag_6 . For the anion, we find a planar C_{2v} lowest energy structure similar to that of the neutral geometry. This isomer has a binding energy of 7.96 eV - only slightly larger than that of the neutral cluster. A tripyramid structure, similar to that of the cation, emerges as the next higher energy structure, fairly close in energy with $\Delta E=0.1$ eV. Other groups [8,13,14] find that the tripyramid structure is the lowest energy isomer of the anion. In fact, the ordering we obtain for the isomers of Ag_6^- is opposite to that obtained in the all-electron DFT [14] study of this system, which finds that the planar structure is 0.06 eV higher in energy than the tripyramid isomer. HF/CI ECP calculations [16] on this system also find the tripyramid structure to be energetically more favorable. Although our calculations favor the planar structure over the tripyramid structure as the likely candidate for the lowest energy isomer, the 3-d isomer appears to be more consistent with photoelectron spectroscopy measurements

of the vertical detachment energies of Ag_6^- . The vertical detachment energy calculated for the planar isomer is 1.48 eV substantially smaller than the observed experimental value [27] of 2.06 ± 0.05 eV - a notable exception to the even-odd alternation trend in the variation of VDEs with cluster size. In fact, this experimental value is closer to our calculated VDE of 2.20 eV for the higher energy tripyramid isomer. The calculated adiabatic electron affinities for the two isomers mentioned are 1.41 eV and 1.59 eV respectively.

3.1.6 Ag_7 , Ag_7^+ , Ag_7^-

The lowest energy structure of Ag_7 is a pentagonal bipyramid. This result is in agreement with the other theoretical studies [13,20] on this system. Hyperfine structure calculations [21] also indicate a pentagonal bipyramid geometry for neutral Ag_7 . The binding energy of this isomer is 9.22 eV. The lowest energy structure of the cation shows the same packing as the neutral and has a binding energy of 11.28 eV. The calculated vertical IP for the pentagonal bipyramid is 6.07 eV (the adiabatic IP is 5.94 eV) continuing the even-odd alternation trend in ionization potential.

We find that a tripyramid-type C_s structure is the lowest energy isomer for the anion, with a binding energy of 10.00 eV. The vertical detachment energy calculated for this isomer is 2.43 eV. The experimentally measured [27] VDE for Ag_7 is 2.55 ± 0.10 eV. However, the authors point out in their paper that the tail on the right shoulder of the photoelectron spectra could be associated with a separate transition, in which case, the vertical detachment energy could be approximately 2.3 eV-2.4 eV, closer to our calculated value of 2.43 eV. The adiabatic EA obtained in our investigations is 2.21 eV.

3.1.7 Ag_8 , Ag_8^+ , Ag_8^-

The silver octamer is remarkable in that all three species - neutral, cation and anion have several isomers that lie very close in energy. The lowest energy isomer of Ag_8 is a T_d structure with a binding energy of 11.32 eV. A dodecahedron D_{2d} structure is only 0.06 eV higher in energy. The Hartree-Fock/CI studies [13] (using a 46-electron ECP) on Ag_8 find the T_d structure to be the lowest energy structure at the Hartree-Fock level, with the D_{2d} structure 0.11 eV higher in energy. However, in the same work, a CI calculation on the Hartree-Fock optimized geometries, reversed this ordering rendering a lower energy D_{2d} structure and a higher energy T_d structure, with an energy difference of $\Delta E = 0.08$ eV. A recent work [20] that employs a tight-binding Hamiltonian finds the D_{2d} isomer to be the lowest energy structure, however, it is not clear whether the T_d structure was investigated in this study.

The lowest energy isomer for the cation is a C_s structure closely related to the highest (fourth) energy isomer of neutral Ag_8 . This observation is in agreement with HF/CI calculations [13] on Ag_8^+ . The three isomers we have obtained for Ag_8^+ - the C_s structure, a C_{2v} structure at $\Delta E = 0.05$ eV, and another (different geometry) C_{2v} structure at $\Delta E = 0.08$ eV - all lie within a very small energy range. We find a binding energy of 12.92 eV for the C_s isomer of Ag_8^+ , a vertical IP of 6.94 eV for the T_d isomer of neutral Ag_8 . The adiabatic ionization potential corresponding to the change in structure from isomer 1 of neutral Ag_8 (T_d structure) to the C_{2v} structure (the third isomer of Ag_8^+), is found to be 6.48 eV.

We find that the lowest energy structure for the anion is a D_{2d} isomer, which has a binding energy of 11.50 eV, comparable to that of the neutral cluster. The second higher energy isomer for Ag_8^- is a close lying double-capped C_{2v} structure with

$\Delta E=0.02$ eV. The third isomer is a C_s structure with $\Delta E=0.06$ eV. Our finding of three isomers of Ag_8^- that are very close in energy is in contrast to the HF/CI calculations on this system, which find that these three isomers lie over a 0.3 eV energy range. The calculated VDE for the D_{2d} isomer is 1.70 eV. The experimental value [27] of the VDE for the Ag_8 cluster is 1.65 ± 0.05 eV. Our calculated adiabatic electron affinity for the D_{2d} isomer is 1.54 eV.

The structural and electronic characteristics (binding energies, ionization potentials, vertical detachment energies and electron affinities) of the lowest energy isomers for Ag_n ($2\leq n\leq 8$) clusters are given in table 2. The trends in binding energies, ionization potentials and electron affinities are shown graphically in Fig. 4. The odd-even trend of ionization energies and electron affinities with respect to cluster size for silver clusters is clearly apparent. The trends of the vertical and adiabatic ionization potentials are similar. The larger differences between vertical and adiabatic IPs correspond to cases where a large structural change occurs on ionization, e.g. in the case of the pentamer and the hexamer, where there is a structural change from the planar geometries of the neutral cluster, to the three-dimensional geometries of the cation. The vertical detachment energies (VDE) and the electron affinities follow each other closely except in the case of Ag_6 , which has been discussed earlier.

TABLE 2. Electronic characteristics of the lowest energy isomers of Ag_n clusters.

Cluster	BE/atom (eV)	IP _v (eV)	IP _a (eV)	VDE (eV)	EA (eV)
Ag_2 Calc. Expt.	0.80 0.825 [†]	7.98 7.56 [†]	7.92 -	1.15 1.06 $\pm$ 0.02 [§]	1.09 -
Ag_3 Calc. Expt.	0.78 0.87 [*]	6.08 6.0 [‡]	5.92 -	2.37 2.43 $\pm$ 0.01 [§]	2.36 2.32 [§]
Ag_4 Calc. Expt.	1.04 -	6.65 6.65 [‡]	6.64 -	1.79 1.65 $\pm$ 0.05 [§]	1.71 -
Ag_5 Calc. Expt.	1.14 -	6.32 6.35 [‡]	6.08 -	2.10 2.11 $\pm$ 0.05 [§]	2.08 -
Ag_6 Calc. Expt.	1.31 -	7.19 7.15 [‡]	6.68 -	1.48, 2.20 2.06 $\pm$ 0.05 [§]	1.41, 1.59 -
Ag_7 Calc. Expt.	1.32 -	6.07 6.40 [‡]	5.94 -	2.43 2.55 $\pm$ 0.1 [§]	2.21 -
Ag_8 Calc. Expt.	1.42 -	6.94 7.10 [‡]	6.48 -	1.70 1.65 $\pm$ 0.05 [§]	1.54 -

* Ref. [23], † Ref. [24], § Ref. [27], ‡ Ref. [29]

There is some disagreement between our work and others [13,15] about whether or not certain structures are minima or not. The root of this disparity lies in the fact that the potential surface of silver clusters is very flat and some of the isomers of Ag_n clusters have very low frequencies associated with them. Although we have used a fine

grid for the energy and frequency calculations in all our investigations, there is room for errors in frequency calculations using different functionals and different ECPs. Hence, a structure thought to be a true minimum in one approach may not be so in another. Indeed, this may be the case for Ag_6^+ and Ag_7^- , where we find that the planar trigonal geometry for the Ag_6^+ cation, and the pentagonal bipyramid for the Ag_7^- anion are each characterized by small negative frequencies (less than 30 cm^{-1} , despite being repeated for various distortions) whereas others [13,15] find these structures to be minima.

Figure 4. The behavior of the binding energies per atom, ionization potentials (vertical and adiabatic), vertical detachment energies and electron affinities, as a function of cluster size.

3.2 $\text{Ag}_3\text{C}_2\text{H}_4$ COMPLEX

We first present and discuss results of our investigations for the C_2H_4 molecule. These are followed by results for the cluster-ligand complex.

3.2.1 C_2H_4 molecule

Our calculations for the C_2H_4 molecule, with double zeta basis sets for C and H, give a C-C distance of 1.35 Å, C-H distances of 1.09 Å and C-C-H angles of 121.6°. These results compare well with the best estimates (1.3307 Å, 1.0809 Å and 121.47° respectively) obtained from high-level ab initio calibration studies [71] on this system. Figure 5 gives the ground state geometry of the C_2H_4 molecule. The binding energy for the ethylene molecule is 24.40 eV compared with the experimental value [71,72] of 23.06 eV. The vertical ionization potential for ethylene is 10.44 eV, substantially larger than that for the silver trimer. Calculations with a double zeta basis on C and a 6-311G++ basis set on H give a binding energy of 24.30 eV and a vertical ionization potential of 10.55 eV. The bond lengths and the bond angles remain essentially the same.

Figure 5. The structure of C_2H_4 .

3.2.2 $\text{Ag}_3\text{C}_2\text{H}_4$ complex

The two stable isomers of the $\text{Ag}_3\text{C}_2\text{H}_4$ complex obtained in our calculations are shown in Fig. 6. Both isomers of the $\text{Ag}_3\text{C}_2\text{H}_4$ complex involve bonding with the Ag_3 plane perpendicular to the C_2H_4 plane, rather than the parallel-plane [73,74] or near parallel-plane [75] configurations predicted for ethylene on silver surfaces. In fact, extensive searches for this configuration ruled out the possibility of an attractive interaction between the cluster and the ligand in this orientation. A possible explanation is that the bonding in the Ag_3 cluster is predominantly s-like, with a small hybridization of the s-orbitals with the $5p_x$ and $5p_y$ orbitals that lie in the plane of the silver cluster. (In this picture, the silver trimer lies in the xy-plane, while the ethylene molecule is in the yz-plane). The $5p_z$ orbitals of silver do not hybridize significantly with the 4s orbitals. As a result of this small sp-hybridization in the plane of cluster, the overlap of these hybridized orbitals with the π -orbitals of ethylene is maximized in a side-on type configuration, thus preferring this to the parallel-plane configuration.

In the lowest energy isomer (isomer 1) for $\text{Ag}_3\text{C}_2\text{H}_4$, the Ag_3 component of the complex has an isosceles triangle structure with sides of length 2.67 Å and an apex angle of 62.5°. The apex silver atom is in turn bonded to the ethylene molecule, with the Ag atom forming the apex of another isosceles triangle with the two carbon atoms, with Ag-C distances of 2.29 Å. The C-C bond length in ethylene increases from 1.35 Å to 1.39 Å with a 12° out-of-plane distortion of the hydrogen atoms. There is little change in the C-H bond lengths or the H-C-H bond angles. The bond-lengths and bond angles of the $\text{Ag}_3\text{C}_2\text{H}_4$ complex are indicated in Fig. 6. The binding energy of the complex (as defined by Eq. 3) for this isomer is 0.82 eV. Zero-point vibrational contributions are neglected in the calculation of the binding energy of the complex, we estimate that these effects contribute less than 0.02 eV to the energy. It is interesting to note that the Ag_3 cluster maintains its isosceles triangle structure, with the two silver atoms that form the base of the triangle moving closer to each other, so that there is a net reduction in the apex angle. The vertical ionization potential for the $\text{Ag}_3\text{C}_2\text{H}_4$ complex (calculated by constraining the cation to the equilibrium geometry of the neutral complex) was found to be 5.72 eV. These results are summarized in table 3. Since the IP_v for ethylene is significantly larger than that for the silver cluster, the loss of the electron takes place primarily from the silver cluster. This is also apparent from the Mulliken charges on the different atoms, which reveals that the loss of an electron upon ionization takes place predominantly from the Ag atoms in the cluster. The reduction in the vertical ionization potential for the silver trimer upon forming a complex with ethylene is 0.36 eV for the lower energy isomer. This net reduction in the vertical IP has been observed in photoionization spectroscopy experiments [50] on the $\text{Ag}_n\text{C}_2\text{H}_4$ ($n=3-7$) system. In particular, a net reduction of approximately 0.4 eV occurs for the $\text{Ag}_3\text{C}_2\text{H}_4$ complex, which agrees well with our theoretical calculations for this isomer. Results for the electronic characteristics of the two configurations of the silver-ethylene complex are given in table 3.

Figure 6. The two isomers for $\text{Ag}_3\text{C}_2\text{H}_4$.

The second (higher energy) isomer has the silver atoms forming an equilateral triangle structure of sides of length 2.70 Å. The bonding in this structure is side-on, with two Ag atoms bonded to the carbon atoms of the ethylene molecule, at Ag-C distances of 2.35 Å. The structural change in ethylene is greater for this isomer - the C-C bond length increases from 1.35 Å to 1.42 Å accompanied by a 28° out-of-plane distortion of the hydrogen atoms. As in the first isomer, there is little change in the C-H bond lengths or the H-C-H bond angles. The binding energy of the complex in the higher energy configuration is 0.47 eV. The vertical ionization potential for isomer 2 is 6.24 eV, i.e. 0.16 eV larger than that for the pure silver trimer.

TABLE 3: Binding Energies and ionization potentials for the two isomers of the $\text{Ag}_3\text{C}_2\text{H}_4$ complex.

Isomer	BE (eV)	IP_v (eV)	IP_a (eV)
Lowest Energy Isomer	0.82	5.72	5.62
Higher Energy Isomer	0.47	6.24	5.26

A graphical representation of the higher energy levels for the non-interacting Ag cluster and ethylene molecule as well as the two isomers of the silver-ethylene complex is given in Fig. 7. A comparison of the highest occupied molecular orbital (HOMO) in the two isomers with the HOMO for bare Ag_3 , reveals that the HOMO in the case of isomer 1 is higher in energy while the HOMO in the case of isomer 2 is lower in energy with regard to Ag_3 . A direct application of Koopman's theorem for the silver component leads to a lowering in the vertical ionization potential of 0.32 eV in the case of isomer 1 of the complex (as compared with the bare silver cluster) and an increase in the IP_v of 0.04 eV in the case of isomer 2. These results are consistent with those obtained from our (more rigorous) calculations for the vertical IP. A comparison of the shift in the molecular orbital energies between the isolated species and the isomers of the cluster-molecule complex shows small shifts in the energies of the inner orbitals, an indication that the charge transfer in the complex is small.

We also examine the magnitude of the charge transfer that occurs in this system as measured indirectly through Mulliken charges as well as the net dipole moment of the complex. While neither in itself is an exact measure of the charge transfer taking place in the system [76], we use a comparison of the two properties for each of the two isomers as a tool to estimate the magnitude of the charge transfer occurring in this system. The Mulliken charge for the lowest energy isomer for the silver-ethylene complex shows a small, negative charge of 0.02 on the cluster. It also has a net dipole moment of 2.35 D (1 au = 2.54 Debye) directed along the two-fold symmetry axis and pointing from the Ag_3 cluster towards the C_2H_4 molecule. This corresponds to a charge transfer of approximately 0.13 electrons (as compared with the 0.02 obtained from Mulliken charge analysis) in a point charge approximation where we use the distance between the centers-of-mass of the ethylene molecule and that of the silver cluster as the effective distance of separation. Mulliken populations for the second isomer show a

small positive charge of 0.04 on the silver cluster. This isomer has a net dipole moment of 1.21 D, pointing from the silver cluster to the ethylene, contrary to the polarity obtained from the Mulliken charges. The effective charge corresponding to this value of the dipole moment is 0.08 electrons, with the charge transfer occurring from ethylene to the silver cluster. It should be noted that the effective distance of separation between the centers-of-mass is larger for isomer 1 (3.70 Å) than that for isomer 2 (3.04 Å). We have also studied the effect of applying a small external electric field (0.01 au in magnitude, directed along the cluster-molecule axis and pointing towards the cluster) on the bond-lengths in the complex. While this does result in an increase in the charge transfer and a larger dipole moment (as could be expected), the overall change in the intra-cluster and cluster-ligand distances is only about 1.5%, which also points [54] to an overall small charge transfer.

Figure 7. A comparison of the highest occupied molecular orbital (HOMO) for Ag_3 , C_2H_4 and the two isomers of $\text{Ag}_3\text{C}_2\text{H}_4$. The HOMOs are denoted by an asterisk.

An interesting question that arises is the origin of the difference between the ionization potentials of the two isomers of the complex. This difference can be explained in terms of the bonding in the system. As mentioned, the bonding between ethylene and the silver cluster is a covalent one with the in-plane sp-hybridized orbitals of the Ag_3 cluster overlapping with the π -orbitals of C_2H_4 . Additionally, there is a very small mixing of the 5s orbitals with the 4d orbitals in the silver cluster. In the lower energy isomer of the complex, the mixing is that of the s orbitals with the d_z^2 orbitals i.e. out of the plane of the silver cluster. In the higher energy isomer there is a slightly larger mixing between the 5s orbitals and the d_{xy} as well as the $d_{x^2-y^2}$ orbitals in the plane of the silver cluster. The d orbitals are repulsive and their presence in the plane of the cluster results in a smaller charge transfer from the ethylene molecule to the silver cluster for isomer 2 (the higher energy isomer of the complex). This explains the larger

ionization potential for the second isomer as well as the larger bond lengths, as compared with the lower energy isomer.

3.3 (AgX)_n CLUSTERS (X=Cl, Br; n≤4)

While silver clusters and silver-ligand systems have been investigated through a large number of theoretical and experimental studies, there is disproportionately little information available - experimental or theoretical - on silver-halide clusters. On the other hand, bulk AgCl and AgBr (which are light-sensitive over a wide spectral range) are fairly well-investigated systems because of their relevance to photography. Both AgCl and AgBr are ionic solids whose structures are similar to that of sodium chloride, with lattice constants of 5.55 Å and 5.77 Å respectively. Mass spectra measurements [53] on non-stoichiometric Ag_nBr_m clusters find that the spectrum is dominated by Ag_nBr_{n-1}⁺ clusters with peaks at n=5, 14, 23 and 32, indicating an exceptional abundance of the clusters for these *n* values. (There is no data available for AgCl clusters). While we will concentrate on stoichiometric (AgX)_n clusters in the sections that follow, our results for (Ag_nBr_n)⁺ cations also explain the reason for the dominance of the Ag_nBr_{n-1}⁺ clusters in the mass spectra.

The geometries of the isomers of (AgCl)_n and (AgBr)_n clusters obtained in our calculations are shown in Fig. 8 and Fig. 9 respectively.

3.3.1 AgCl and AgBr

AgCl cluster. The diatomic AgCl has a silver-chlorine bond length of 2.36 Å. This is substantially smaller than the distance of 2.78 Å between the ions in bulk AgCl. The experimental value [77] for the bond in the gas phase diatomic AgCl molecule is 2.28 Å. Examination of the highest occupied molecular orbitals reveals covalent as well as ionic contributions to this bond, with significant overlap between the s-d hybridized Ag orbitals and the p orbitals of Cl. A Mulliken charge analysis for AgCl gives an effective charge of +0.5 on Ag and -0.5 on Cl for the diatom case. While Mulliken charges are not reliable as tools to measure the absolute ionicity in these systems, they are useful in analyzing the trends in bonding within a series of clusters. The calculated binding energy of the AgCl pair is 3.08 eV as compared with the experimental [77] one of 3.40 eV. To put this value of the bond strength into perspective, it should be noted that our calculated value for the binding energy of the Ag₂ dimer is 1.60 eV. It is also useful to compare this value with the cohesive energy for bulk silver chloride. The cohesive energy in ionic solids is usually expressed in terms of ion pairs. For bulk AgCl this value is 9.27 eV/ion pair. We present all our results in terms of AgCl pairs (the molecule rather than the ion pair). To obtain the binding energy per AgCl molecule for bulk AgCl, we would need to subtract the IP for the Ag atom from the sum of the cohesive energy for AgCl and the electron affinity for Cl. Using a value of 7.57 eV for the IP of the Ag atom, and 3.62 eV for the electron affinity of Cl, we obtain a binding energy per AgCl pair of 5.32 eV for bulk silver chloride. The vertical IP for AgCl is 9.66 eV, and the adiabatic IP of 9.44 eV corresponds to a longer bond length of 2.72 Å in (AgCl)⁺.

AgBr cluster. The Ag-Br bond length and binding energy/AgBr pair obtained for the diatom are 2.45 Å and 2.90 eV respectively. These compare well with the experimental results [77] of 2.39 Å and 2.97 eV respectively. The bulk binding energy per AgBr pair is 4.92 eV, given a cohesive energy of 9.12 eV/ion pair for silver bromide and using a value of 3.37 eV for the electron affinity of Br. The bonding in AgBr cluster is

very similar to that in AgCl and a Mulliken charge analysis for this diatom gives effective charges of ± 0.47 for the constituent entities. The calculated vertical IP for the AgBr cluster is 9.29 eV, with the adiabatic IP of 9.12 eV corresponding to a rearrangement to an Ag-Br bond distance of 2.78 Å in (AgBr)⁺.

3.3.2 (AgCl)₂ and (AgBr)₂

(AgCl)₂ cluster. (AgCl)₂ is a rhombus with Ag-Cl bond distances of 2.62 Å. The shorter diagonal of the rhombus has two silver atoms at its ends separated by a distance of 3.08 Å. This separation is significantly larger than typical Ag-Ag distances of 2.5 Å to 2.8 Å seen for pure silver clusters. The two Cl atoms in this cluster are 4.23 Å apart. The binding energy of (AgCl)₂ is 4.08 eV/AgCl pair as compared with 3.08 eV for the AgCl cluster. A Mulliken charge analysis for this cluster gives effective charges of +0.38 on Ag and -0.38 on Cl. The vertical IP for (AgCl)₂ is 9.24 eV. The geometry of the cation (AgCl)₂⁺ is also a rhombus. The Ag-Cl distance of 2.67 Å in the cation is only marginally different from the neutral case but with a dramatic change in the Ag-Ag and Cl-Cl distances. The two Ag atoms in the cation are 4.45 Å apart and lie on the longer diagonal of the rhombus (in the neutral, they formed the shorter side), while the Cl atoms now lie on the shorter diagonal at 2.96 Å. The rearrangement energy corresponding to this rather significant structural change is 0.4 eV - the difference between the vertical and adiabatic IPs of this cluster.

(AgBr)₂ cluster. The (AgBr)₂ cluster is also a rhombus with Ag-Br bond length of 2.69 Å. The binding energy per AgBr pair for (AgBr)₂ is 3.97 eV. The shorter diagonal of the rhombus has two silver atoms at its ends at 2.99 Å separation, while the Br atoms are 4.46 Å apart. The calculated vertical IP for the (AgBr)₂ cluster is 9.34 eV and the adiabatic IP is 0.44 eV lower at 8.90 eV. As in (AgCl)₂, there is a reversal of the Ag-Ag and Br-Br distances in the rhombus structure of the cation. Mulliken charges for (AgBr)₂ also show a trend similar to that of the silver chloride cluster with effective charges of +0.31 and -0.31 on Ag and Br respectively.

3.3.3 (AgCl)₃ and (AgBr)₃

(AgCl)₃ cluster. The (AgCl)₃ cluster is a planar ring shaped structure. The inner silver atoms are arranged in the form of an isosceles triangle, but it should be noted that the Ag-Ag distances for this triangular arrangement are 3.34 Å and 3.56 Å, and are not representative of Ag-Ag bonding. Cl atoms are outside of this triangular core with Ag-Cl distances of 2.53 Å and 2.55 Å. The binding energy per AgCl pair for this cluster is 4.48 eV, continuing the upward trend in this quantity with increasing cluster size. The charge analysis for this cluster gives average Mulliken charges (this structure has inequivalent atoms) of +0.33 for the Ag atoms, and -0.33 for Cl atoms. The vertical ionization energy of (AgCl)₃ is 9.81 eV. There is little change in the interatomic separation of Ag and Cl in the cation, the overall ring geometry of the neutral cluster is unchanged upon ionization. However, the Ag atoms in the cation are far from bonding distances of each other, with average Ag-Ag distances of 4.02 Å. The adiabatic IP for the cluster is 8.86 eV, corresponding to a rearrangement energy of 0.39 eV.

(AgBr)₃ cluster. The structure of (AgBr)₃ is also a planar ring structure - similar to that of (AgCl)₃, the only difference in this case is that the three Ag atoms form a smaller equilateral triangle core with Ag-Ag distances of 3.28 Å. Br atoms are outside this Ag core with Ag-Br distances of 2.60 Å. The binding energy per AgBr pair for this cluster is 4.39 eV. The Mulliken charges for this cluster are +0.27 for the Ag atoms, and -0.27 for Br atoms. The vertical ionization energy for (AgBr)₃ is 9.64 eV. The cation also

has a ring shaped packing, and there is little change in the Ag-Br distances on ionization. Unlike the case of the $(\text{AgCl})_3$ cation, the change in the Ag-Ag distances on ionization is less dramatic, and the adiabatic IP for the cluster is only 0.16 eV smaller than the vertical IP.

Figure 8. The isomers of $(\text{AgCl})_n$ clusters ($1 \leq n \leq 4$).

3.3.4 $(\text{AgCl})_4$ and $(\text{AgBr})_4$

For each of the sizes of $(\text{AgX})_n$ clusters described so far, only one isomer emerged as a stable isomer despite conducting several gradient-based searches for optimal geometries, starting with different symmetric and non-symmetric configurations. While we do not claim that no other isomers exist for the smaller clusters, our searches (though extensive) have been unsuccessful in obtaining other structures. For the $n=4$ clusters however, we find two isomers both of which are 3-dimensional.

$(\text{AgCl})_4$ cluster. The two isomers we obtain for $(\text{AgCl})_4$ lie 0.6 eV apart in energy. The lower energy isomer can be visualized as a distorted cube-like structure. The Ag-Cl distances in this isomer are 2.74 Å, while the four Ag atoms are 3.42 Å apart. This isomer has a BE/pair of 4.64 eV. The second isomer of $(\text{AgCl})_4$ is a 3-dimensional capped relative of the ring-shaped two dimensional $(\text{AgCl})_3$ one. This isomer has a

binding energy/AgCl pair of 4.49 eV, comparable to the BE/pair of 4.48 eV for $(\text{AgCl})_3$. The Mulliken charges obtained are +0.23 for Ag and -0.23 for Cl in isomer 1, and +0.30 to +0.36 for Ag and -0.28 to -0.32 for Cl in isomer 2. The vertical IP calculated for the $(\text{AgBr})_4$ clusters are 9.00 eV and 8.96 eV for isomers 1 and 2 respectively, and the adiabatic IPs are 8.86 eV and 8.71 eV respectively. There is little change between the neutral and cation geometries upon ionization.

Figure 9. The isomers of $(\text{AgBr})_n$ clusters ($1 \leq n \leq 4$).

(AgBr)₄ cluster. The two isomers of $(\text{AgBr})_4$ once again follow a pattern similar to that of $(\text{AgCl})_4$, with some noteworthy differences. The lowest energy isomer is once again a distorted cube-like structure, the distortion is more pronounced in the case of $(\text{AgBr})_4$ than for $(\text{AgCl})_4$. Second, the Ag-Br bond lengths in $(\text{AgBr})_4$ are 2.82 Å and the Ag-Ag bond lengths are 3.25 Å. The difference between the bond distances of these two species is less pronounced than in $(\text{AgCl})_4$ and while a Ag-Ag distance of 3.25 Å does not necessarily promote strong metal-metal bonds, this type of bonding is certainly of more significance in $(\text{AgBr})_4$ as compared with $(\text{AgCl})_4$. The BE/pair for this isomer is 4.51 eV, with calculated Mulliken charges of +0.21 for Ag and -0.21 for Br. The second isomer is 0.52 eV higher in energy, and has a structure related to the planar structure of $(\text{AgBr})_3$ and has a BE/pair of 4.38 eV. The effective charges of Ag and Br

for this isomer range from +0.22 to +0.26 for Ag, to -0.2 to -0.27 for Br. We obtain vertical IPs of 9.17 eV and 9.04 eV, and adiabatic IPs of 9.02 and 8.88 eV for the first and second isomers of $(\text{AgBr})_4$ respectively. There is little change in the structure of either of the isomers on ionization, consistent with the fact that the rearrangement energies in the two cases are 0.15 eV and 0.16 eV respectively.

3.3.5 $(\text{Ag}_n\text{Br}_{n-1})^+$ mass spectra

Last, we examine the likely reason for the dominance of $(\text{Ag}_n\text{Br}_{n-1})^+$ clusters in the mass spectra of non-stoichiometric Ag_nBr_m clusters [53] in terms of the energy required to detach a Br from the rest of the cluster, once the cluster is ionized. We study the series of $(\text{AgBr})_n^+$ clusters ($n \leq 4$), and calculate the energy required to detach a Br atom from each of these clusters. We find that while the energy required to detach a Br atom from neutral $(\text{AgBr})_2$ is 4.1 eV, only 1.0 eV is required to disassociate $(\text{AgBr})_2^+$ into Ag_2Br and Br fragments. Our results for the detachment energy of a single Br atom from the $(\text{AgBr})_n^+$ series are summarized below.

This low detachment energy for Br (from the stoichiometric ionized cluster) is consistent with observations of $(\text{Ag}_n\text{Br}_{n-1})^+$ dominated mass spectra for Ag_nBr_m clusters, and our calculations on $(\text{Ag}_n\text{Cl}_{n-1})^+$ indicate a similar behavior for other silver-halide clusters as well.

Key features of the structural and electronic characteristics of $(\text{AgX})_n$ clusters are summarized in table 4.

TABLE 4. Calculated binding energies and effective charges for $(\text{AgX})_n$ clusters. Average values of the Mulliken charges are given for clusters with inequivalent atoms.

Cluster	BE/AgCl (eV)	BE/AgBr (eV)	Mulliken Charges (e^-)	
			Ag, Cl	Ag, Br
AgX	3.08	2.90	0.50, -0.50	0.47, -0.47
$(\text{AgX})_2$	4.08	3.97	0.38, -0.38	0.31, -0.31
$(\text{AgX})_3$	4.48	4.39	~ 0.33 , -0.33	~ 0.27 , -0.27
$(\text{AgX})_4$	4.64, 4.49	4.51, 4.38	~ 0.30 , -0.30	~ 0.25 , -0.25

4. Summary

Bonding in silver clusters is dominated by the 5s electrons, accounting for a preponderance of cluster structures similar to that of alkali metals, especially for the lowest energy isomers. This, in part, explains the success that one valence electron ECP based studies [1,13,16] have had in obtaining many of the lowest energy isomers found in our study. The semi-core p and d-electrons do however have significant hybridization effects which can be important. Our investigations as well as those of other groups show that the energy landscape of small Ag_n clusters is rather flat. Replacing the semi-core electrons with ECPs (in the very large core ECP calculations) causes a lack of directionality in binding due to the absence of the semi-core d-orbitals. The difficulty of accurately locating and characterizing minima (local and global) and saddle-points on this flat potential energy is compounded when semi-core p and d electrons are replaced with large core ECPs.

In the preceding sections we presented results of our investigations of the interaction of silver trimer with an ethylene molecule. Two isomers were identified for the $\text{Ag}_3\text{C}_2\text{H}_4$ complex, both of which involve bonding in an orientation where the metal cluster plane is perpendicular to the plane of the ethylene molecule. The preference for this configuration is explained in terms of the overlap of the sp-hybridized orbitals of the cluster with the π -orbitals of ethylene. The strength of the interaction between the cluster and the molecule is significant, and the bonding between the silver cluster and the ethylene molecule is predominantly covalent with binding energies of 0.82 eV and 0.47 eV for the two isomers. (It should be noted that the binding energy of the silver trimer is 2.33 eV or 0.78 eV/atom). We found a decrease of 0.37 eV in the calculated vertical ionization potential (as compared with the pure silver cluster) for the lower energy configuration of the $\text{Ag}_3\text{C}_2\text{H}_4$ complex, which agrees well with experimental observations on this system. We also find a small increase in the vertical IP for the higher energy isomer and have explained this in terms of the details of the bonding in the system.

Our calculations for stoichiometric $(\text{AgCl})_n$ and $(\text{AgBr})_n$ clusters show that the bonding in these clusters is strongly dominated by the Ag-X ($X=\text{Cl}, \text{Br}$) interaction, with Ag-Ag distances larger in AgCl clusters than in AgBr clusters. We also find that the bonding in $(\text{AgBr})_n$ clusters is less ionic than in $(\text{AgCl})_n$ clusters. There is evidence of significant overlap between the s-d hybridized orbitals and the halide p orbitals, indicative of some covalent contribution to the bonding. The isomers we obtain for $(\text{AgX})_2$ and $(\text{AgX})_3$ are planar, and three-dimensional isomers make their appearance for $n=4$ in these clusters with the beginning of cube-type structures. The binding energy/pair for the $(\text{AgX})_n$ clusters show a monotonic rise in the range studied reaching 85% of their bulk value by $n=4$. Finally, we explain the observed dominance of $(\text{Ag}_n\text{Br}_{n-1})^+$ clusters in the mass spectra of non-stoichiometric Ag_nBr_m clusters in terms of the energy required to detach a Br from the rest of the ionized cluster.

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6. References

1. Flad, J., Igel-Mann, G., Preuss, H., and Stoll, H. (1984) A combination of pseudopotentials and density functionals: results for Cu_n , Cu_n^+ , and Ag_n^+ clusters ($n \leq 4$), *Chem. Phys.* **90**, 257-269.
2. Flad, J., Igel-Mann, G., Preuss, H., and Stoll, H. (1985) Comparison of group IA and group IB homonuclear clusters, *Surface Science* **156**, 379-385.
3. Walch, S.P., Bauschlicher, C.W., and Langoff, S.R. (1986) Theoretical studies of diatomic and triatomic systems containing the group IB atoms Cu, Ag, and Au, *J. Chem. Phys.* **85**, 5900-5907.
4. Walch, S.P. (1987) A theoretical study of the excited states of Ag_3 , *J. Chem. Phys.* **87**, 6776-6778.
5. Balasubramanian, K. and Liao, M.Z. (1988) Electronic states and potential energy surfaces of gold and silver trimers, *Chem. Phys.* **127**, 313-324.
6. Balasubramanian, K. and Feng, P.Y. (1989) The ionization potentials of Ag_n and Au_n and binding energies of Ag_n , Au_n , Ag_n^+ , Ag_n and Au_n^+ ($n=1-4$), *Chem. Phys. Lett.* **159**, 452-458.
7. Bauschlicher, C.W., Langoff, S.R., and Partridge, H. (1989) Theoretical study of the structures and electron affinities of the dimers and trimers of the group IB metals (Cu, Ag, and Au), *J. Chem. Phys.* **91**, 2412-2419.
8. Partridge, H., Bauschlicher, C.W., and Langoff, S.R. (1990) Theoretical study of the positive ions of the dimers and trimers of the group IB metals (Cu, Ag, and Au), *Chem. Phys. Lett.* **175**, 531-535.
9. Bauschlicher, C.W., Langoff, S.R., and Partridge, H. (1990) Theoretical study of the homonuclear tetramers and pentamers of the group IB metals (Cu, Ag, and Au), *J. Chem. Phys.* **93**, 8133-8137.
10. Ramirez-Solis, A., Daudey, J.P., Novaro, O., and Ruiz, M.E. (1990) Nonadditivity and stability of Ag_3 . A multireference configuration interaction study, *Z. Phys. D - Atoms, Molecules and Clusters* **15**, 71-78.
11. Das, K.K. and Balasubramanian, K. (1991) Electron affinities of Ag_4 and Au_4 , *Chem. Phys. Lett.* **176**, 571-574.
12. Liao, D.W. and Balasubramanian, K. (1992) Electronic structure of Cu_6 , Ag_6 and Au_6 , and their positive ions, *J. Chem. Phys.* **97**, 2548-2552.
13. Bonai-Koutecký, V., Cepiva, L., Fantucci, P., and Koutecký, J. (1993) Effective core potential-configuration interaction study of electronic structure and geometry of small neutral and cationic Ag_n clusters: predictions and interpretation of measured properties, *J. Chem. Phys.* **98**, 7981-7994.
14. Kaplan, I.G., Santamaria, R., and Novaro, O. (1993) Theoretical study of the geometric structures and energetic properties of anionic clusters Ag_n^- ($n=2-6$), *Int. J. of Quant. Chem. Symp.* **27**, 743-753.
15. Kaplan, I.G., Santamaria, R., and Novaro, O. (1994) A comparative theoretical study of stable geometries and energetic properties of small silver clusters, *Chem. Phys. Lett.* **218**, 395-400.
16. Bonai-Koutecký, V., Cepiva, L., Fantucci, P., Pittner, J., and Koutecký, J. (1994) Effective core potential-configuration interaction study of electronic structure and geometry of small anionic Ag_n^- clusters - predictions and interpretation of photodetachment spectra, *J. Chem. Phys.* **100**, 490-506.

17. Kaplan, I.G., Santamaria, R., and Novaro, O. (1993) Non-additive forces in atomic clusters: The case of Ag_n , *Molecular Physics* **84**, 105-114.
18. Garzon, I.L., Kaplan, I.G., Santamaria, R., and Novaro, O. (1997) Ab initio model potential and molecular dynamics simulations of Ag_6 clusters, *Z. Phys. D - Atoms, Molecules and Clusters* **40**, 202-205.
19. Warken, M. and Bonai-Koutecký, V., (1997) Quantum mechanical treatment of stationary and dynamical properties of bound vibrational systems: application to the relaxation dynamics of Ag_5 after an electron photodetachment, *Chem. Phys. Lett.*, **272**, 284-294.
20. Poteau, R., Heully, J.-L. and Spiegelmann, F., (1997) Structure, stability, and vibrational properties of small silver clusters, *Z. Phys. D - Atoms, Molecules and Clusters* **40**, 479-482.
21. Arratia-Pérez, R., Hernández-Acevedo, L., and Alvarez-Thon, L. (1998) Calculated paramagnetic hyperfine structure of pentagonal bipyramid Ag_7 cluster, *J. Chem. Phys.* **108**, 5795-5798.
22. Garzon, I.L., Kaplan, I.G., Santamaria, R., and Novaro, O. (1998) Molecular dynamics study of the Ag_6 cluster using ab initio many-body potential, *J. Chem. Phys.* **109**, 2176-2184.
23. Hilpert, K. and Gingerich, K.A. (1980) Atomization enthalpies of the molecules Cu_3 , Ag_3 , and Au_3 , *Ber. Bunsenges. Phys. Chem.* **84**, 739-745.
24. Morse, M.D. (1986) Clusters of transition-metal atoms, *Chem. Rev.* **86**, 1049-1109.
25. Cheng, P.Y. and Duncan, M.A. (1988) Vibronic spectroscopy and dynamics in the jet-cooled silver trimer, *Chem. Phys. Lett.* **152**, 341-346.
26. Hopkins, J.B., Langridge-Smith, P.R.R., Morse, M.D., and Smalley, R. unpublished results quoted in Ref. 7.
27. Ho, J., Erwin, K.M., and Lineberger, W.C. (1990) Photoelectron spectroscopy of metal cluster anions: Cu_n^- , Ag_n^- , and Au_n^- , *J. Chem. Phys.* **93**, 6987-7002.
28. Simard, B., Hackett, P.A., James, A.M., and Langridge-Smith, P.R.R. (1991) The bond length of silver dimer, *Chem. Phys. Lett.* **186**, 415-422.
29. Jackschath, C., Rabin, I., and Schulze, W. (1992) Electron impact ionization of silver clusters Ag_n , $n \leq 36$, *Z. Phys. D - Atoms, Molecules and Clusters* **22**, 517-520.
30. Alameddine, G., Hunter, J., Cameron, D., and Kappes, M.M., (1992) Electronic and geometric structure in silver clusters, *Chem. Phys. Lett.* **192**, 122-128.
31. Ellis, A.M., Robles, E.S.J., and Miller, T.A. (1992) Dispersed fluorescence spectroscopic study of the ground electronic state of silver trimer, *Chem. Phys. Lett.* **210**, 132-140.
32. Harbich, W., Fedrigo, S., and Buttet, J., (1993) The optical absorption spectra of small silver clusters ($n=8-39$) embedded in rare gas matrices, *Z. Phys. D - Atoms, Molecules and Clusters* **26**, 138-140.
33. Fedrigo, S., Harbich, W., and Buttet, J., (1993) Optical response of Ag_2 , Ag_3 , Au_2 , and Au_3 in argon matrices, *J. Chem. Phys.* **99**, 5712-5717.
34. Wedum, E.E., Grant, E.R., Cheng, P.Y., Willey, K.F., and Duncan, M.A., (1994) On the assignment of Jahn-Teller effects in the ultraviolet absorption spectrum of Ag_3 , *J. Chem. Phys.* **100**, 6312-6318.

35. Leisner, T., Rosche, Ch., and Woste, L. (1996) The catalytic role of small coinage-metal clusters in photography, *Surface Review and Letters* **3**, 1105-1108.
36. Wolf, S., Sommerer, G., Rutz, S., Schreiber, E., Leisner, T., Wöste, L., and Berry, R.S. (1995) Spectroscopy of size-selected neutral clusters: Femtosecond evolution of neutral silver trimers, *Phys. Rev. Lett.* **74**, 4177-4180.
37. Tiggesbäumker, J., Koller, L., and Meiwes-Broer, K.-H. (1996) Bound-free collective electron excitations in negatively charged silver clusters, *Chem Phys. Lett.* **260**, 428-432.
38. Haslett, T.L., Bosnick, K.A., and Moskovits, M. (1998) Ag_5 is a planar trapezoidal molecule, *J. Chem. Phys.* **108**, 3453-3457.
39. Voge, H.H. and Adams, C.R. (1967) Catalytic oxidation of olefins, *Advan. Catalysis* **17** (1967) 151-221.
40. Carter, E.A. and Goddard III, W.A. (1989) Chemisorption of oxygen, chlorine, hydrogen, hydroxide, and ethylene on silver clusters: A model for the olefin epoxidation reaction, *Surf. Sci.* **209**, 243-289.
41. Boussard, P.J.E., Seigbahn, P.E.M., and Svensson, M. (1994) The interaction of ammonia, carbonyl, ethylene and water with the copper and silver dimers, *Chem. Phys. Lett.* **231**, 337-344.
42. Belanzoni, P., Rosi, M., Sgamellotti, A., Baerends, E.J., and Floriani, C. (1996) On the electronic structure and bonding of the polynuclear aryl derivatives of the group 1B metals $\text{Cu}_5(\text{C}_6\text{H}_5)_5$, $\text{Ag}_4(\text{C}_6\text{H}_5)_4$ and $\text{Au}_5(\text{C}_6\text{H}_5)_5$ by density functional theory, *Chem. Phys. Lett.* **257**, 41-48.
43. Ma, N.L., Ng, K.M., and Tsang, C.W. (1997) Theoretical studies of the structure and stability of $\text{Ag}(\text{C}_6\text{H}_5)_n^+$ ($n=1$ and 2), *Chem. Phys. Lett.* **277**, 306-310.
44. Ma, N.L. (1998) How strong is the Ag^+ -ligand bond?, *Chem. Phys. Lett.* **297**, 230-238.
45. Willey, K.F., Cheng, P.Y., Bishop, M.B., and Duncan, M. A. (1991) Charge-transfer photochemistry in ion-molecule cluster complexes of silver, *J. Am. Chem. Soc.* **113**, 4721-4728.
46. Duncan, M.A. (1993) Spectroscopy and photochemistry in clusters and organometallic complexes of silver, in M.A. Duncan(eds) *Advances in Metal and Semiconductor Clusters*, JAI Press Inc., Greenwich, pp. 123-157.
47. Rayner, D.M., Lian, L., Fournier, R., Mitchell, S.A., and Hackett, P.A. (1995) Thermal and photodesorption from a molecular surface: Ammonia on Ag_2 , *Phys. Rev. Lett.* **74**, 2070-2073; Mitchell, S.A., Lian, L., Rayner, D.M., and Hackett, P.A. (1996) Photodissociation of Cu_2NH_3 and Ag_2NH_3 , *J. Phys. Chem.* **100**, 15708-15715.
48. Koretsky, G.M. and Knickelbein, M.B. (1997) Infrared photodissociation spectroscopy of $\text{Ag}_n(\text{C}_6\text{H}_6)_m$ and $\text{Ag}_n(\text{C}_6\text{D}_6)_m$ clusters: Evidence of adsorption-induced symmetry reduction in benzene, *Chem. Phys. Lett.* **267**, 485-490.
49. Reddic, J.E., Robinson, J.C., and Duncan, M.A. (1997) Growth and photodissociation of $\text{Ag}_x\text{-C}_{60}$ cation complexes, *Chem. Phys. Lett.* **279**, 203-208.
50. Koretsky, G.M. and Knickelbein, M.B. (1997) The reactions of silver clusters with ethylene and ethylene oxide: Infrared and photoionization studies of $\text{Ag}_n(\text{C}_2\text{H}_4)_m$, $\text{Ag}_n(\text{C}_2\text{H}_4\text{O})_m$ and their deuterated analogs, *J. Chem. Phys.* **107**, 10555-10566.

51. Knickelbein, M.B. and Koretsky, G.M. (1998) Infrared studies of the interaction of methanol with Cu_n , Ag_n , and Au_n , *J. Phys. Chem.* **102**, 580-586.
52. Koga, T., Aoki, H., and Tatewaki, H. (1995) Why do the second row transition metal atoms prefer $5s^1 4d^{m+1}$ to $5s^2 4d^m$? , *Theor. Chim. Acta* **92**, 281-295.
53. Rabin, I., Jackschatch, Schulze W., and Froben, F.W. (1991) Silver-halogen cluster compounds Ag_nX_m ($n \geq 2$, $0 \leq m \leq n$, $\text{X} = \text{F}, \text{Br}$), *Z. Phys. D - Atoms, Molecules and Clusters* **19**, 401-404.
54. Pachioni, G., Bagus, P.S., and Philpott, M.R., (1989) Cluster-model study of the interaction of halogen atoms with Ag clusters, *Z. Phys. D - Atoms, Molecules and Clusters* **12**, 543-546.
55. Flad, J., Stoll, H., Nicklass, A., and Preuss, H. (1990) Quantum chemical calculations of the latent image formation. III. Adsorption of Ag^+ , Ag_n and Ag_n^- ($n \leq 2$) on a (100) silver bromide surface, *Z. Phys. D - Atoms, Molecules and Clusters* **15**, 79-86.
56. Bagatur'yants, A.A., Safonov, A.A., and Shelimov, K.B. (1993) Ab initio calculations of M-centers on the AgBr surface (100); Primary Ag_2 center formation, *Russian Jour. of Phys. Chem.* **67**, 72-78.
57. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Gill, P.M.W., Johnson, B.G., Robb, M.A., Cheeseman, J.R., Keith, T., Petersson, G.A., Montgomery, J.A., Raghavachari, K., Al-Laham, M.A., Zakrzewski, V.G., Ortiz, J.V., Foresman, J.B., Cioslowski, J., Stefanov, B.B., Nanayakkara, A., Challacombe, M., Peng, C.Y., Ayala, P.Y., Chen, W., Wong, M.W., Andres, J.L., Replogle, E.S., Gomperts, R., Martin, R.L., Fox, D.J., Binkley, J.S., Defrees, D.J., Baker, J., Stewart, J.P., Head-Gordon, M., Gonzalez, C., and Pople, J. A. (1995) Gaussian 94, Revision C.4, Gaussian, Inc., Pittsburgh PA.
58. Russo, T.V., Martin, R.L., and Hay, P.J. (1995) Effective core potentials for DFT calculations, *J. Phys. Chem.* **99**, 17085-17087.
59. Van Wullen, C. (1996) On the use of common effective core potentials in density functional calculations. I. Test calculations on transition-metal carboxyls, *Int. Jour. Quant. Chem.* **58**, 147-152.
60. Becke, A.D. (1988) Density functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* **38**, 3098-3100.
61. Perdew, J.P. and Wang, Y. (1992) Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B* **45**, 13244-13249.
62. Becke, A.D. (1993) Density-functional thermochemistry III. The role of exact exchange, *J. Chem. Phys.* **98**, 5648-5652.
63. Lee, C., Yang, W., and Parr, R.G. (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* **37**, 785-789.
64. Miehlich, B., Savin, A., Stoll, H., and Preuss, H. (1989) Results obtained with the correlation energy density functionals of Becke and Lee, Yang and Parr, *Chem. Phys. Lett.* **157**, 200-206.
65. Andrae, D., Häußermann, U., Dolg, M., Stoll, H., and Preuß, H. (1990) Energy-adjusted ab initio pseudopotential for the second and third row transition elements, *Theor. Chim. Acta* **77**, 123-141.
66. Hay, P.J. and Wadt, W.R. (1985) Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg, *J. Chem. Phys.* **82**, 270-283.

67. Godbout, N., Salahub, D.R., Andzelm, J., and Wimmer, E. (1992) Optimization of Gaussian-type basis sets for local spin density functional calculations. Part I. Boron through neon, optimization technique and validation, *Can. J. Chem.* **70**, 560-571.
68. Perdew J.P. (1986) Density-functional approximation for the correlation energy of the inhomogeneous electron gas, *Phys. Rev. B* **33**, 8822-8824.
69. Dunning, Jr. T.H., (1970) Gaussian basis functions for use in molecular calculations. I. Contraction of (9s5p) atomic basis sets for the first-row atoms, *J. Chem. Phys.* **53**, 2823-2833. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.
70. Schlegel, H.B. (1987) Optimization of equilibrium geometries and transition structures, in K.P. Lawley (eds), *Ab initio Methods in Quantum Chemistry Part-I*, John Wiley & Sons, Chichester, pp. 249-286.
71. Martin, J.M.L. and Taylor, P.R. (1996) Geometry, vibrational frequencies, and total atomization energy of ethylene: A calibration study, *Chem. Phys. Lett.* **248**, 336-344.
72. Chase Jr., M.W., Davies, C.A., Downey Jr., J.R., Frurip, D.J., McDonald, R.A., and Syverud, A.N. (1985) *JANAF thermochemical tables, 3rd Ed.* *J. Phys. Chem. Ref. Data* **14**, Suppl. I.
73. Backx, C. and de Groot, C.P.M. (1982) Electron energy loss spectroscopy of ethylene on Ag(110) precovered with oxygen: Energy dependence of the cross section, *Surf. Sci.* **115**, 382-394.
74. Arvanitis, D., Baberschke, K., Wenzel, L., and Döbler, U. (1986) Experimental study of the chemisorbed state of C₂H₂, C₂H₄, and C₂H₆ on noble-metal surfaces, *Phys. Rev. Letts.* **57**, 3175-3178.
75. Solomon, J.L., Madix, R.J., and Stöhr, J. (1982) Orientation of ethylene and propylene on Ag(110) from near edge X-ray adsorption fine structure, *J. Chem. Phys.* **93**, 8379-8382.
76. Nelín, C. J., Bagus, P. S., and Philpott, M. R. (1987) The nature of the bonding of CN to metals and organic molecules, *J. Chem. Phys.* **87**, 2170-2178.
77. Gaydon, A.G. (1968) Dissociation energies and spectra of diatomic molecules, Chapman and Hall, London.

D_{3h}

D_{2h}

D_{2d}

C_{2v}

C_{5v}

C_s

(a)

(b) $\Delta E = 0.52$ eV