THE IONIZATION POTENTIALS OF $Ag_n$ AND $Au_n$ AND BINDING ENERGIES OF $Ag_n$, $Au_n$, $Ag^+_n$ AND $Au^+_n$ ($n=1-4$)

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The ionization potentials and binding energies of gold and silver clusters and their positive ions containing up to four atoms are investigated using a complete active space MCSCF followed by multi-reference singles + doubles CI which included up to 1.9 million configurations. The ionization potentials for both $Au_n$ and $Ag_n$ as a function of cluster size $n$ exhibit an interesting "saw-tooth" behavior. The total binding energies of both the clusters and ions as a function of size reveal that the tetramers of gold and silver exhibit unusual stabilities. The gold clusters in general have larger AE and IPs in comparison to silver clusters due to relativistic effects.

1. Introduction

The properties of gold and silver clusters have been the topics of many investigations in recent years [1-21]. A recent review by one of the authors (KB) [1] on coinage metal clusters summarizes the progress in experimental and theoretical investigations of these clusters.

The theoretical interest in a comparative study of gold and silver clusters arises from the dramatic difference in the bonding of gold clusters in comparison to silver clusters [17-21]. The relativistic effects are substantially larger for gold clusters leading to enhanced bonding and shorter metal-metal bonds in gold clusters in comparison to silver clusters.

The experimental investigations [2-16] of gold and silver clusters include many studies such as ESR spectra of matrix-isolated clusters, Raman and visible spectra, negative photoelectron spectra and the vibronic spectra of jet-cooled clusters.

Smalley and coworkers [3-5] have recorded the photoelectron spectra of $Cu_n^-$, $Ag_n^-$ and $Au_n^-$ as a function of cluster size. These spectra have revealed interesting information on the excited electronic states of the neutral clusters as well as the electron affinities (EA) of these clusters as a function of size. The electron affinities of all the three coinage metal clusters reveal interesting odd-even alternations characterized by saw-tooth-type patterns that have not yet been fully understood.

Cheng and Duncan [13] have recently obtained the vibronic spectra and dynamics of jet-cooled $Ag_3$. Two-color excimer + dye laser experiment on $Ag_3$ revealed that the $Ag^+_3$ signal was found to be featureless. The vertical ionization potential of $Ag_3$ was predicted to be less than 6 eV based on the combined laser energies.

The binding energies of the dimer and trimer of gold and silver have been obtained by Hilpert and Gingerich [16] using high-temperature mass-spectroscopic methods. The theoretical investigations made up to now have not provided accurate binding energies for these species due to large d correlation effects. For example, the CASSCF/POLCI calculations [18] which included d correlation effects in a limited manner yielded an atomization energy of 62 kcal/mol for $Au_3$ in comparison to an experimental value of 88 kcal/mol. The binding energies of the tetramers have not yet been measured experimentally.

The objective of this investigation is to compute accurately the ionization potentials and binding energies of $Ag_n$ and $Au_n$ for $n$ up to 4 using a com-
plete active space MCSCF followed by multi-reference singles+doubles CI (MRSDCI) which include up to 1.9 million configurations. It is well known that it is difficult to calculate the ionization potentials, electron affinities and binding energies in exact agreement with experiment using ab initio methods. However, the relative trends of the properties as a function of cluster size seem to be in very good agreement with the experiment. In this investigation, we calculate these properties, explain the experimentally observed patterns and predict the properties of the tetramer which are not known experimentally at present. The binding energies of the positive ions are also obtained and compared with neutral clusters and with experimental results when available.

2. Method of calculations

We employ the general method of complete active space MCSCF followed by multi-reference singles+doubles CI (MRSDCI) including the d electrons to study the ionization potentials and binding energies. All calculations employed relativistic effective core potentials [22,23] which retained the outer d^{10}s^{1} shells of the silver and gold atoms in the active space. A (3s3p3d) valence Gaussian basis set was uniformly employed for all the four clusters.

The dimer, trimer and tetramer calculations included 22, 33 and 44 electrons. The positive ions included one electron less than the corresponding number of electrons for the neutral species. The CASSCF calculations of the dimer and trimer included 22 and 33 electrons, respectively, in the active space. The trimer included 7 a_{1} orbitals, 5 b_{2} orbitals, 3 b_{1}, and 3 a_{2} orbitals in the active space. It was found for the trimer that single+double excitations of the d shells are more important than the inclusion of the d orbitals in the active space. Thus, for the tetramer, the excitations from the d shells were not allowed in the CASSCF but the d orbitals were allowed to relax for both the neutral and ionic species.

The CI calculations done were based on multi-reference singles+doubles CI (MRSDCI). The MRSDCI calculations included all the configurations in the CASSCF with coefficients $\geq 0.07$ as reference configurations. Then single+double excitations were allowed from the reference configurations. The CI calculations of the dimer and trimer included all the 22 and 33 electrons, respectively. The CI calculations of the dimer and trimer ions included 21 and 32 electrons, respectively. The CI calculations of the tetramer included the most important 32 electrons. Those orbitals with energy eigenvalues $< -0.512$ hartree were kept in core in that excitations were not allowed from these. A previous investigation [21] on the electronic states of Au$_{4}$ revealed that this approximation is quite satisfactory. The large-scale MRSDCI calculations on these clusters included up to 1.9 million configurations and thus the contracted CI (CCI) method of Siegbahn was employed for the large-scale CI calculations.

The geometries of the neutral trimer clusters were obtained before by Balasubramanian and Liao [18] using the CASSCF/RMRSDCI method. These geometries were used for full MRSDCI of the neutral and ionic species. The optimized CASSCF/CI ground state geometry of Ag$_{4}$ and Au$_{4}$ was used to compute the vertical IPs and ionization energies of these clusters. For Ag$_{4}$, this corresponds to a rhombus structure with the side of the rhombus being 2.87 Å and the acute Ag–Ag–Ag angle 55.5°. The corresponding geometry of Au$_{4}$ in the 1A$_{1}$ state is a rhombus with the side bond length being 2.69 Å and the acute Au–Au–Au angle 58.6°.

The atomization energies of all the clusters were obtained by making comparable CASSCF/CI calculations for a linear geometry with all M–M bond lengths set to 8.0 Å. This method ensures size consistency in the calculations of atomization energies. All the CASSCF/MRSDCI calculations were done using the modified version of ALCHEMY II codes of one of the authors (KB) [24] to include relativistic ECPs (RECPs). The CCI calculations were done using Siegbahn’s CCI codes modified for the Cray XMP-48 system at the San Diego supercomputing center.

3. Results and discussions

Table 1 shows the vertical ionization potentials of

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# The major authors of ALCHEMY II are B. Lengsfield, B. Liu and M. Yoshimine.
Table 1
Ionization potentials in eV of Ag\(_n\) and Au\(_n\).

<table>
<thead>
<tr>
<th>Species</th>
<th>IP (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>theory uncorrected (^\ast)</td>
</tr>
<tr>
<td>Au</td>
<td>8.57</td>
</tr>
<tr>
<td>Au(_3)</td>
<td>8.78</td>
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<tr>
<td>Au(_4)</td>
<td>6.26</td>
</tr>
<tr>
<td>Au(_5)</td>
<td>6.82</td>
</tr>
<tr>
<td>Ag</td>
<td>6.73</td>
</tr>
<tr>
<td>Ag(_2)</td>
<td>6.7</td>
</tr>
<tr>
<td>Ag(_3)</td>
<td>5.31</td>
</tr>
<tr>
<td>Ag(_4)</td>
<td>5.75</td>
</tr>
</tbody>
</table>

\(^\ast\) CASSCF/MRSDCI uncorrected value.

\(^b\) Corrected for errors in the IPs due to basis set and electron correlation errors by comparing the IPs of the atoms with experiment.

Ag\(_n\) and Au\(_n\) (n = 1–4) while fig. 1 shows the actual plot of the ionization energies. First we discuss the individual IPs and compare with the known experimental values.

The experimental ionization potentials of gold and silver atoms from Moore’s atomic tables of energy levels [25] are 7.57 and 9.22 eV, respectively. As seen from table 1, the corresponding theoretical values are 6.73 and 8.57 eV, respectively. Thus, there is 11.1% and 7% atomic correlation and basis set errors in the IPs of the two atoms. As mentioned in section 1, absolute agreement in the IPs, EAs (electron affinities) and AEs of these species between experiment and theory is not expected even at the present level of ab initio treatment. However, it is the relative trend that we seek to compare with the experiment. The atomic correlation error was applied to the calculated vertical IPs in table 1 uniformly to all the species (about 11.1% for silver clusters and 7% for gold clusters). The corrected values are found to be in remarkable agreement with experimental results.

The experimental IPs of Ag\(_2\) and Au\(_3\) appear to be known, although for gold clusters experimental IPs have not yet been measured. Smalley and coworkers [26] in an unpublished work obtained the IP of Ag\(_2\) as 7.56 eV. This value is in very good agreement with our corrected theoretical value of 7.44 eV, where the correction is for atomic correlation effects.

Cheng and Duncan [13] obtained the IP of Ag\(_3\) as less than 6 eV using excimer + dye laser experiments. As mentioned before, the Ag\(_2^+\) signal was found to be featureless with an appearance potential of less than 6 eV estimated based on combined laser energies. This value is in very good agreement with our corrected theoretical value of 5.9 eV. The present value is much improved compared to Walch’s IP for Ag\(_3\) of 4.8 eV [27].

Based on the good agreement between the corrected theoretical results and the experimental results on Ag\(_2\) and Ag\(_3\), we predict the IPs of Au\(_2\), Au\(_3\) and Au\(_4\) to be 9.4±0.2, 6.7±0.2 and 7.3±0.3 eV, respectively. The experimental IPs of these species are not known at present. Similarly, the IP of Ag\(_4\) is predicted to be 6.4±0.3 eV.

As seen from fig. 1, the IPs of Ag\(_n\) and Au\(_n\) (n = 1–4) exhibit saw-tooth patterns reminiscent of the patterns seen by Smalley and coworkers [3] for the electron affinities of these clusters. The even clusters, namely, M\(_2\) and M\(_4\) have closed-shell \(^1\)A\(_2\) electronic ground states. In the case of the dimer, the ionization leads to an open-shell \(^2\)Σ\(_g^+\) ground state; the ionization process involves removal of an electron from the \(\sigma\) bonding orbital, which is doubly occupied for the neutral dimer. Thus, ionization of the dimer leads to destabilization since the process destroys a closed-shell bonding orbital. Consequently, the ionization potential of the dimer is noticeably higher than the trimer or the atom. For the tetramer, the ground state is described by the \(^1\)A\(_g\) closed-shell ground state in \(D_{2h}\) symmetry. The tetramer ion has a \(^3\)B\(_{1u}\) ground state which is obtained by removing
an electron from the highest doubly occupied $b_{1u}$ orbital. The exact nature of this orbital will be discussed later. Once again, ionization of the tetramer leads to destabilization of the closed-shell ground state and hence higher ionization potential in comparison to the trimer.

The trimers of gold and silver have two nearly degenerate electronic states of $^2B_2$ and $^2A_1$ symmetry [18]. These two are Jahn-Teller components of the same $^2E'$ state. The $^2B_2$ state is slightly lower than the $^2A_1$ state for both Ag$_3$ and Au$_3$. The removal of the $b_2$ electron (singly occupied) leads to a $^1A_1$ closed-shell ground state. Thus, the trimers have substantially lower IPs compared to the dimer and tetramer. However, the difference in the IPs of the dimers and trimers is larger than the difference in the IPs of trimers and tetramers. This could be because the ionization of the dimer involves removal of the $\sigma^*$ bonding electron while the ionization of tetramer involves removal of an electron from the $b_{1u}$ orbital which is not a strongly bonding orbital.

Table 2 shows the atomization energies of Ag$_n$ and Au$_n$ as a function of $n$. The atomization energy is defined as the energy for the following process:

$$M_n \rightarrow nM(^2S)$$

In Table 2, we also show the experimental values when available. The experimental results were obtained from high-temperature mass-spectroscopic measurements of Hilpert and Gingerich [16]. Fig. 2 shows the plots of both the experimental and theoretical AEs and the binding energies per atom. Although the AE of the trimers was obtained before using CASSCF/POLCI method [18], the present values are substantially improved since they are obtained using a full CASSCF/MRSDCI method which included up to 3 million CSFs. Thus, the present AEs for Ag$_3$ and Au$_3$ (48 and 76 kcal/mol) are much improved in comparison to the previous CASSCF/POLCI [18] values of 35 and 62 kcal/mol, respectively.

The $D_e$'s reported in table 2 for Ag$_2$ and Au$_2$ are the best theoretical values obtained to date ($D_e$(Ag$_2$) = 31 kcal/mol, $D_e$(Au$_2$) = 46 kcal/mol). The previous CASSCF/restricted MRSDCI $D_e$'s obtained by Balasubramanian and Liao [18] are 27 and 38.7 kcal/mol, respectively. In these calculations, only the d shell electrons in the A$_1$ block were correlated, whereas in the present calculations MRSDCI of all the 22 electrons of the dimer are done. The present $D_e$'s are also substantially improved in comparison to the theoretical values ($D_e$(Ag$_2$) = 25 kcal/mol and $D_e$(Au$_2$) = 36 kcal/mol obtained by Ross and Ermler [28]. Consequently, it is clear that d cor-
relation effects account for considerable fraction of the binding energies of these clusters. Even the best calculations do not give exactly the experimental values due to RECPs, basis set limitations and electron correlation errors. However, the relative trend for the clusters as a function of size mimics the experimental trend. A comparison of the theoretical $D_e$ of the dimers with experiment reveals about 10% correlation error per Ag atom and 6.6% correlation error per Au atom. If this correction is applied to the theoretical values for the trimers, the agreement with the experiment is remarkable. For example, the corrected theoretical AEs of Ag$_2$ and Au$_2$ are 62 and 91 kcal/mol, respectively. These values are within 2–3 kcal/mol of the experimental values (i.e. within the uncertainties of the experimental results).

The above discussion clearly indicates that the AEs of the tetramers of the two clusters can be predicted within experimental uncertainties. The above corrections when applied to the AEs of the tetramers in table 2 we obtain $A\varepsilon(Ag_4) = 170\pm 15$ kcal/mol and $A\varepsilon(Au_4) = 200\pm 10$ kcal/mol. The value for Au$_4$ is plotted in fig. 2 as predicted experimental value.

As seen from fig. 2, the theoretical trend even without the correction for missing electron correlations mimics the experimental trend for the binding energies as a function of cluster size. The binding energies per atom also exhibit similar patterns. For example, Au$_4$ has about 50 kcal/mol binding energy per atom while Au$_3$ has 29 kcal/mol binding energy per atom. Note that Au$_3$ has a binding energy of 26.5 kcal/mol per atom which compares well with the trimer. Consequently, among the smaller clusters, tetramers exhibit unusual stability. For the silver clusters, BE/atom are 19.5 kcal/mol for the dimer, 20 kcal/mol for the trimer and 42.5 kcal/mol for the tetramer. Again, Ag$_4$ is unusually more stable among the smaller clusters.

We also calculated the binding energies of some of the ionic clusters to compare with experiments. The theoretical MRSDCI $D_e$ of Au$_2^+$ and Ag$_2^+$ were obtained by subtracting CI energies at $R_e$ and 8.0 Å. The values obtained this way for Au$_2^+$ and Ag$_2^+$ are 1.79 and 1.30 eV, respectively. The corrected (theoretical) $D_e$'s of Au$_2^+$ and Ag$_2^+$ are 2.03 and 1.56 eV, respectively. The experimental $D_e^0(Ag_2^+)$ is $1.66\pm 0.05$ eV [26]. As seen from table 2, the uncorrected theoretical $D_e$ of Ag$_2$ (1.34 eV) is almost the same as the $D_e$ of Ag$_2^+$ (1.30 eV). This supports the experimental finding of Smalley and coworkers [26] that the $D_e$ of Ag$_2^+$ should be very close to the $D_e$ of Ag$_2$. In the case of Au$_2$, however, the uncorrected theoretical dissociation energies are $D_e(Au_2) = 2.0$ eV and $D_e(Au_2^+) = 1.79$ eV. Thus the neutral dimer is more strongly bound in comparison to the ion.

We also obtained the atomization energies of the M$_n^+$ ions from the AEs of the neutral species and the IPs of the metal atoms using the following formula:

$$AE(M_n^+) = IP(M) - IP(M_n) + AE(M_n).$$

The above formula can be easily verified using simple energy diagrams. This formula is, however, more strictly valid for adiabatic IPs than for vertical IPs. However, the differences between the vertical and adiabatic IPs are not very substantial and thus the AEs predicted by this formula should be reasonable.

Table 3 shows the theoretical (corrected and uncorrected) values obtained using this formula and the corresponding experimental values for Ag$_2^+$ and Ag$_3^+$.

<table>
<thead>
<tr>
<th>Species</th>
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<th>Expt.</th>
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<td></td>
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<tr>
<td>Au$_3^+$</td>
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<tr>
<td>Au$_4^+$</td>
<td>215</td>
<td>244</td>
<td></td>
</tr>
</tbody>
</table>

a) Obtained using the formula $AE(M_n^+) = IP(M) - IP(M_n) + AE(M_n)$.
b) Direct experimental value from ref. [26].

As seen from table 3, the corrected theoretical values are in remarkable agreement with experimental results for the Ag$_2^+$ and Ag$_3^+$ ions. For Ag$_2^+$, it is in-
teresting to note that the direct photodissociation value obtained by Smalley and coworkers [26] is in remarkable agreement with the value obtained by using the above formula.

In comparing table 2 with table 3, we find that the stability of Ags and Ags⁺ are about the same while Au⁺ is somewhat less stable in comparison to Au₂. The trimers ions, on the contrary are more stable than the neutral species. For example AE(Ag⁻) = 99 kcal/mol while AE(Ags) = 62 kcal/mol. Again, Ag⁺ and Au⁺ are more stable than the corresponding neutral clusters. In all cases Au⁺ cluster ions are more stable than Ag⁺ ions due to relativistic effects.

Next, we compare the silver and gold clusters. As seen from fig. 1, the observed saw-tooth pattern is repeated for both gold and silver clusters almost in a parallel manner. However, the IPs of gold clusters are consistently higher than the silver clusters. This is mainly because of relativistic mass–velocity stabilization of the outer 6s orbital of the gold atom. Since the highest occupied orbital of every cluster is predominantly made of the 6s orbital of the gold atom, the highest occupied orbital of Auₙ is much more stabilized in comparison to the corresponding orbital of Agₙ. Consequently, the IPs of Auₙ are larger than the corresponding values for Agₙ.

We consider next the nature of the highest occupied orbitals for the neutral and ionic tetrameric species. Table 4 shows the coefficients of the highest occupied MRSDCI natural orbitals of M₄ and M₄⁺. As seen from this table, this orbital is of b₁u symmetry in the D₄h point group of rhombus although in the Cᵥ group it has a₁ symmetry. For Au₄, this orbital is predominantly made of the 6s orbital of the metal atoms located on the z axis. The participation of the d orbitals of the gold atoms is non-negligible although it is not shown in table 4. For the rhombus structure, the atoms on the z axis are more separated in comparison to the atoms located on the y axis. Thus, this orbital should be considered non-bonding but slightly antibonding along the z axis. For Ag₄, however, the participation of the 5p₂ orbitals of the atoms located on the y axis becomes quite significant (see table 4). Thus this highest occupied b₁u orbital is more bonding for Ag₄. Thus the difference in the IPs of Ag₄ and Ag₅ (0.44 eV) is smaller than the corresponding difference in the IPs of Au₄ and Au₅ (0.56 eV).

As seen from table 4, the orbital relaxation effects are non-negligible for both the clusters. That is, the coefficients of the orbitals of the neutral and ionic species are not nearly the same. Consequently, approximate methods of predicting the IPs such as Koopmans’ theorem cannot yield good IPs for these clusters.

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>Au⁺</th>
<th>Au₄</th>
<th>Ag₄</th>
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<td>0.337</td>
<td>0.139</td>
<td>0.149</td>
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<td>-0.351</td>
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<tr>
<td>M₄s₁</td>
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<td>-0.337</td>
<td>-0.139</td>
<td>-0.149</td>
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<tr>
<td>M₄s₂</td>
<td>0.416</td>
<td>0.358</td>
<td>0.140</td>
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<tr>
<td>M₄s₃</td>
<td>0.329</td>
<td>0.351</td>
<td>0.320</td>
<td>0.331</td>
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<tr>
<td>M₂z₁</td>
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<td>M₂z₂</td>
<td>-0.107</td>
<td>-0.170</td>
<td>-0.150</td>
<td>-0.047</td>
</tr>
</tbody>
</table>

ₐ M₁ and M₄ are the two atoms located on the z axis of the rhombus structure. M₂ represents the linear combination of the two atoms located on the y axis. The labels s₁, s₂, and s₃ are used for the s basis functions, while z₁ and z₂ are the labels for the p₂ functions.

4. Conclusion

In this investigation we studied the ionization potentials and binding energies of Agₙ, Auₙ, Ag⁺ₙ and Au⁺ₙ (ₙ = 1–4). The ionization potentials as a function of size exhibit interesting saw-tooth patterns. The corrected theoretical IPs and the theoretical trends are in excellent agreement with the known experimental results. The atomization energies (AEs) as a function of cluster size reveal that the tetramer of both gold and silver have unusually large binding energies per atom. The corrected theoretical IPs and the theoretical trends are in excellent agreement with the known experimental results. The atomization energies (AEs) as a function of cluster size reveal that the tetramer of both gold and silver have unusually large binding energies per atom. The corrected theoretical CASSCF/MRSDCI atomization energies of the dimers and trimers are in excellent agreement with the known experimental results. The binding energies of the positive ions are also computed. The Dₑ of Ag⁺ was found to be close to Ag₂ while the Dₑ of Au⁺ was found to be smaller than the Dₑ of Au₂. The positive ions of larger clusters were in general found to have larger AEs than the neutral clusters.

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References