The Oblate Structure and Unexpected Resistance in Reactivity of Ag\textsubscript{15}\textsuperscript{+} with O\textsubscript{2}.

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Abstract. Theoretical studies have been carried out to investigate the unusual reactivity of Ag\textsubscript{15}\textsuperscript{+} cations with oxygen. Our previous work has shown that the reactivity of free metal clusters with oxygen entails a spin excitation that causes reduced reactivity in clusters with filled electronic shells and large HOMO-LUMO gaps. Earlier experiments on Ag\textsubscript{15}\textsuperscript{+} have shown that the cluster exhibits remarkable resistance to reactivity with oxygen despite having a valence electron count that is not expected to result in a filled electronic shell within the spherical jellium model. It is shown that Ag\textsubscript{15}\textsuperscript{+}, Ag\textsubscript{14}, and Ag\textsubscript{13}\textsuperscript{-} clusters with 14 valence electrons, all have oblate bilayer atomic structures that lead to a splitting of the superatomic D-shell in a manner analogous to crystal field splitting of d-states in transition metals. The importance of the oblate structure is demonstrated by showing a correlation between an oblate deformation coefficient and the HOMO-LUMO gap of the different structures of Ag\textsubscript{15}\textsuperscript{+}. The oblate deformation results in the splitting of the electronic subshells and leads to an unusually large HOMO-LUMO gap and the unusual resistance of the cationic species to oxidation.

1. Introduction

The interaction of oxygen with metal clusters has attracted considerable attention as the reactivity pattern in small clusters can be different from the bulk and strongly dependent on the size.\textsuperscript{1-19} These differences arise primarily due to two reasons. Firstly, the electronic states in small symmetric clusters are grouped into electronic shells such as 1S, 1P, 1D, 2S, 1F, 2P, much in the same way as in atoms, and clusters containing 2, 8, 18, 20, 34, and 40 valence electrons correspond to filled shells.\textsuperscript{20-22} The shell structure was first seen through the experimental mass spectra in beams that showed marked peaks, usually referred to as magic numbers, at these sizes.\textsuperscript{20} Later experiments also confirmed that the electronic shells govern the chemical reactivity and clusters having filled shells are generally less reactive to a variety of gases.\textsuperscript{24} Secondly, the reactivity with oxygen is particularly interesting as the ground state of oxygen is a spin triplet with lowest unoccupied orbitals having a spin minority character. Activation of the O-O bond to promote reactivity requires a filling of the minority spin states. As suggested previously by the present authors, the spin conservation in free reacting clusters requires a spin excitation of the cluster to conserve the total spin, as the O-O bond is activated. Consequently, for a variety of anionic clusters, the reactivity with oxygen in even electron systems is found to be less than in odd electron systems.\textsuperscript{3,4,9,10,19} More significantly, the reactivity in even electron clusters with singlet ground states is found to be governed by the difference between the highest
occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This is because a spin excitation of clusters can be looked upon as a promotion from the singlet to the triplet configuration via the transfer of an electron in HOMO to the LUMO of opposite spin. Hence, the reactivity with oxygen not only probes the filled shells but also provides an indirect measure of the gap between the filled and unfilled electronic spectrum.

We have previously examined the reactivity of silver cluster anions with oxygen in a joint theory and experimental undertaking. The experiments revealed variable reactivity with clusters containing an even number of electrons generally exhibiting lower reactivity than those with an odd number of electrons. In particular, Ag$_{13}^-$ appeared as a stable species both in the mass spectra of unreacted species and after exposure to molecular oxygen. This was surprising since Ag is monovalent and Ag$_{13}$ has 14 valence electrons and that does not correspond to a filled electronic shell in a spherically confined nearly free electron gas. We demonstrated that this behavior was rooted in the atomic structure of the clusters that was significantly different from a spherical shape. In fact, the cluster had a bi-layer arrangement. Our studies showed that the large deformation of the spherical shape to a bilayer atomic structure induced a splitting of the delocalized valence electron orbitals into 1S$^2$ $|$ 1P$^4$ $|$ 1P$^2$ 2S$^2$ 1D4 $|$ 1D6 $|$ shells where the vertical lines indicate the gaps between the filled orbitals and the double vertical line indicates the gap between filled and unfilled orbitals. Such a deformation induced splitting resembles the crystal field splitting of the atomic orbitals and shows that the geometry of the cluster may have a profound effect on the reactivity of a cluster with other oxidants. These and other previous studies have all focused on anionic species.

In this work, we extend our studies to include cationic silver clusters. Brechignac and co-workers have examined the reactivity of nitrogen and oxygen to silver cluster cations containing up to 27 atoms in order to examine the physio- and chemisorptions of the oxygen. Their results indicate that while molecular absorption is favored below 77K, above 105 K, the chemisorptions changes into oxidation of the cluster. One of the striking findings was the lack of reactivity of Ag$_{15}^+$ cluster, which had the lowest O$_2$ absorption rates in Ag$_n^+$ for n=10-25. Since the cluster has the same number of valence electrons as Ag$_{13}^-$, it raises the question if the lack of reactivity could also be due to atomic structure. In this work we perform theoretical investigations into silver clusters containing 14 valence electrons to examine if the strong oblate distortion, similar to that of Ag$_{13}^-$, may also explain the stability of Ag$_{15}^+$. Our theoretical studies focus on the role of the geometric deformation of the Ag$_{15}^+$ cluster and its effect on the electronic structure including a comparison with Ag$_{14}$ and Ag$_{13}^-$. The key issue is to examine the atomic structure and to see if the electronic states in all three 14 valence electron systems are marked by large deformations that make all these clusters non-reactive towards oxidation.

2. Methods

A first-principles molecular orbital approach was used wherein the cluster wave function was expressed as a linear combination of atomic orbitals centered at the atomic sites and the exchange correlation effects were included within a generalized gradient density functional theory (DFT) formalism. The actual calculations were carried out using deMon2k set of computer codes. For the exchange and correlation functionals, we used a generalized gradient approximation (GGA) functional as proposed by Perdew, Burke, and Ernzerhof (PBE). The silver atoms were described using a 19 electron quasi-relativistic effective core potential (QECP) with a corresponding valence basis set as proposed by Andrae et al. The auxiliary density was expressed in a combination of primitive Hermite Gaussian functions by using the GEN-A2* auxiliary function set. To determine the geometry and spin multiplicity of the ground states, the configuration space was sampled by starting from several initial configurations and spin multiplicities and then optimizing the geometric structures via the quasi-Newton Levenberg-Marquardt method. All structures were fully optimized in delocalized redundant coordinates without imposing any symmetry constrains to allow for full variational freedom. Previous studies have produced a large library of geometries for neutral silver clusters, and these methods have been successful in identifying the structure of free and ligand protected silver clusters.
To parameterize the geometry of the clusters, a deformation coefficient, $\Delta$, was calculated to determine the planarity of the structures. Note that this is a variation on previous coefficients that were used for primarily prolate clusters. For a given set of coordinates, $\Delta$ is defined as

$$\Delta = \frac{2Q_x}{Q_y + Q_z}$$

and $Q_x$, $Q_y$, and $Q_z$ are the eigenvalues of the deformation tensor

$$Q_{ij} = \sum I R_I R_{ij}$$

in which $I$ runs over every ion, and $R_I$ is the $i$th coordinate of ion $I$, and $R_{ij}$ is the $j$th coordinate of ion $I$ relative to the center of mass. This produces a $3 \times 3$ matrix, and the eigenvalues are ordered so that $Q_z > Q_y > Q_x$. A roughly spherical cluster will have $Q_z \approx Q_y \approx Q_x$ and a $\Delta = 1$. An oblate structure will have $Q_z \approx Q_y > Q_x$, and as the oblate distortion becomes completely planar $\Delta = 0$, while a prolate cluster will have $Q_z > Q_y \approx Q_x$.

3. Results

To understand the observed resistance to oxidation of the Ag$_{15}^+$ cluster, we first performed theoretical studies to identify the cluster’s ground state geometry. The structure, relative energy and HOMO-LUMO gap of a number of local minima of Ag$_{15}^+$ are shown in Figure 1. The lowest energy structure, 1, has a HOMO-LUMO gap of 1.20 eV, significantly larger than that of the other structures, and is quite large for a cluster that has a non-magic number of valence electrons. The structure of 1 is oblate, and the eigenvalues of the deformation tensor are given in Table 1. For comparison, we also list the relevant values for the higher energy structures of Ag$_{15}^+$ as well as for Ag$_{14}$ and Ag$_{13}$ $^-$.

![Figure 1](image)

**Figure 1.** Geometry, relative energy, and HOMO-LUMO gap of different structures of the Ag$_{15}^+$ cluster.
geometries is that the deformation splits the subshell of delocalized orbitals so that the HOMO-LUMO gap is enhanced, resulting in enhanced stability.

To test our hypothesis that geometric factors play an important role in the energetic and electronic stability of Ag\(_{15}^+\), we have plotted the relative stability of the Ag\(_{15}^+\) clusters versus their HOMO-LUMO gaps in Figure 2. The result reveals that the most stable cluster, 1, has the largest HOMO-LUMO gap by a wide margin, and a general trend in that clusters with larger HOMO-LUMO gaps are generally correlated with higher stability. While this agrees with conventional wisdom, that a large HOMO-LUMO gap results in enhanced stability, in the case of clusters which have a nonmagic number of electrons, there is potentially a tradeoff between the energy of cost of the deformation versus the enhanced stability caused by the increased HOMO-LUMO gap. In some systems, such as CuAl\(_{12}\),\(^{10,43}\) the cluster is icosahedral with a quite small gap because the reconstruction energy is too large despite other isomers having a larger HOMO-LUMO gap.

Table 1. Eigenvalues of the deformation tensor, deformation coefficient \(\Delta\), and HOMO-LUMO Gap.

| Cluster | \(Q_x\) | \(Q_y\) | \(Q_z\) | \(\Delta\) | Gap (eV) |
|---------|---------|---------|---------|-----------|---------|
| Ag\(_{15}^+\) (1) | 14.50 | 64.63 | 64.66 | 0.22 | 1.22 |
| Ag\(_{14}^+\) | 13.78 | 54.88 | 56.61 | 0.25 | 1.12 |
| Ag\(_{13}^-\) | 12.90 | 45.77 | 69.53 | 0.22 | 1.28 |
| Ag\(_{15}^+\) (2) | 17.97 | 58.08 | 64.74 | 0.29 | 0.78 |
| Ag\(_{15}^+\) (3) | 15.22 | 55.92 | 71.54 | 0.24 | 0.76 |
| Ag\(_{15}^+\) (4) | 15.98 | 59.97 | 66.54 | 0.25 | 0.88 |
| Ag\(_{15}^+\) (5) | 29.67 | 39.04 | 68.74 | 0.55 | 0.61 |
| Ag\(_{15}^+\) (6) | 28.56 | 45.78 | 60.87 | 0.54 | 0.57 |
| Ag\(_{15}^+\) (7) | 28.28 | 43.26 | 68.9 | 0.50 | 0.54 |
| Ag\(_{15}^+\) (8) | 32.15 | 35.33 | 70.34 | 0.61 | 0.78 |
| Ag\(_{15}^+\) (9) | 29.21 | 34.01 | 72.54 | 0.55 | 0.70 |
| Ag\(_{15}^+\) (10) | 30.02 | 42.37 | 63.72 | 0.57 | 0.44 |
| Ag\(_{15}^+\) (11) | 28.81 | 34.17 | 75.68 | 0.52 | 0.72 |
| Ag\(_{15}^+\) (12) | 31.31 | 31.42 | 74.35 | 0.59 | 0.73 |

We next plotted the HOMO-LUMO gap versus \(\Delta\), the deformation coefficient defined in equation 1, in Fig 3. A notable correlation is seen between the deformation coefficient and the HOMO-LUMO gap. Isomer 1 has both the lowest \(\Delta\) and the largest HOMO-LUMO gap, further demonstrating that a geometric effect has a significant effect on the electronic stability of the Ag\(_{15}^+\) clusters. A low value of \(\Delta\) indicates that the clusters are more oblate, with the spread along the shortest coordinate axis being much lower than the spread along the other two axes. This shows that clusters whose geometry are closest to planar with a strong oblate deformation are the one’s that have the largest HOMO-LUMO gap. This offers evidence that the large electronic stability of Ag\(_{15}^+\) lies in its geometry.

We next analyze the electronic structure of the Ag\(_{15}^+\) cluster, along with that of Ag\(_{14}^+\) and Ag\(_{13}^-\) for comparison. For the purpose of a shell model analysis, we consider Ag\(_{15}^+\) as having 14 valence electrons. Each Ag atom contributes its 5s\(^1\) electron, and the localized 4d orbitals are excluded. Therefore, all three clusters are considered to have 14 valence electrons. Ag\(_{13}^-\) has been found to have an unusually large HOMO-LUMO gap among the anion clusters, and an enhanced resistance to
oxygen etching.\textsuperscript{4} Ag\textsubscript{14} is found to have a relatively large HOMO-LUMO gap for a cluster with a non-magic number of electrons.\textsuperscript{35} Fig 4 shows the geometry and electronic structure of the three clusters with 14 valence electrons. The side view of the geometry shows that all three clusters have an extreme oblate distortion. All three clusters have 4 orbitals with delocalized character within 0.6 eV of the HOMO, and all four orbitals may be assigned as a 2S orbital, a 1P orbital, and 2 1D orbitals. These orbitals are inconsistent with the ordering predicted by the Jellium model, which should order as $|1S\rangle|1P\rangle|1D\rangle|2S\rangle$. Instead the electronic structure is found to be $|1S\rangle|1P\rangle|1D\rangle|1P\rangle|1D\rangle|2S\rangle|1D\rangle|1F\rangle$, where the observed gaps are indicated by vertical lines, and the gap between HOMO and LUMO is indicated by a double vertical line. These results indicate that a splitting of the subshells is observed in Ag\textsubscript{15}\textsuperscript{+}, Ag\textsubscript{14}, and Ag\textsubscript{13}. We have found that the subshells of the spherical jellium model have experienced significant splitting, and the cluster geometry has a strongly oblate distortion for all three electronically stable Silver clusters with 14 valence electrons.

The lowest energy structure of Ag\textsubscript{15}\textsuperscript{+} may be described as an oblate structure which is severely squashed along one axis. The effect of such a deformation on the electronic structure may be qualitatively predicted using concepts from crystal field theory. As shown in Fig. 5, we begin with the spherical jellium model, and we will only consider the 1P, 1D and 2S orbital whose splitting are likely to play a role in a 14 valence electron cluster. We will next consider a strong oblate distortion along the z axis, destabilizing all orbitals which extend along that axis. First, we find that the 1P\textsubscript{x} and 1P\textsubscript{y} orbitals are slightly stabilized, but the 1P\textsubscript{z} orbital is destabilized and is now nearly a frontier orbital. Next we consider the splitting of the 1D orbitals and find that the D\textsubscript{xy} and D\textsubscript{x^2-y^2} orbitals are most stable. The D\textsubscript{yz} and D\textsubscript{zx} orbitals are pushed up in energy due to their extension along the z axis, and the D\textsubscript{z^2} orbital is pushed up most in energy and is almost completely destabilized. Lastly, the 2S\textsuperscript{2}

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**Figure 2.** The HOMO-LUMO Gap and relative total energy of various structures of Ag\textsubscript{15}\textsuperscript{+}.

**Figure 3.** The HOMO-LUMO gap and a deformation coefficient ($\Delta$) plotted against each other.
orbital is only weakly affected by the strong oblate distortion and is expected to be a frontier or near frontier orbital. We note here that the 2S and the D_{z^2} orbital are both of the same symmetry group in an oblate distortion such that they hybridize. Next we compare our predicted splitting with the actual molecular orbitals in Ag_{15}^+. We find that our intuitive model gives effectively the same electronic structure as is found in Ag_{15}^+. The 1P_z orbital is pushed up to be 0.42 eV below the HOMO, consistent with the expected increase in energy. The D_{xy} and D_{x^2-y^2} orbitals both lie 0.48 eV below the HOMO and are the most stable 1D orbitals. The HOMO is found to be a 2S orbital. The LUMOs are found to be the 1D_{xz} and 1D_{yz} orbitals at 1.22 and 1.23 eV above the HOMO. The destabilized 1D_{z^2} is pushed up to 2.68 eV above the HOMO as predicted by the cluster crystal field theory.

Figure 4. Geometry (Top view and side view) and electronic structure of Ag_{15}^+, Ag_{14}, and Ag_{13}^−. The orbitals with significant contributions from the Ag 5s orbitals are assigned subshells, while 4d orbitals are marked in gray.
To further test our hypothesis that a strong oblate distortion will result in silver clusters with 14 valence electrons having a large HOMO-LUMO gap through the similar splitting, we have extended our molecular orbital analysis to Ag$_{14}$ and Ag$_{13}^{-}$ in Fig. 6. We find that the electronic structure of Ag$_{14}$ and Ag$_{13}^{-}$ is nearly the same as that of Ag$_{15}^{+}$. The 1P$_{z}$ orbital is pushed up to be 0.63 eV below the HOMO in Ag$_{14}$ and 0.41 eV below the HOMO of Ag$_{13}^{-}$, both of which are consistent with the splitting caused by the strong oblate distortion. The D$_{xy}$ and D$_{x^2-y^2}$ orbitals lie 0.27 eV and 0.20 eV below the HOMO in Ag$_{14}$, and is the HOMO and a second orbital 0.01 eV below the HOMO in Ag$_{13}^{-}$. The HOMO of Ag$_{14}$ is found to be a 2S orbital, while in Ag$_{13}^{-}$ it lies 0.46 eV below the HOMO. The LUMOs are found to be the 1D$_{xz}$ and 1D$_{yz}$ orbitals at 1.12 and 1.18 eV above the HOMO for Ag$_{14}$, and 1.28 and 1.52 eV above the HOMO in Ag$_{13}^{-}$. The destabilized 1D$_{z^2}$ is pushed up to 2.28 eV above the HOMO in both the Ag$_{14}$ and Ag$_{13}^{-}$ clusters. The splitting of the 1P, 1D, and 2S orbitals in the Ag$_{15}^{+}$, Ag$_{14}$, and Ag$_{13}^{-}$ cluster may all thus be explained by the strong oblate distortion which opens up a large HOMO-LUMO gap, resulting in an unusually electronically stable cluster with a nonmagic number of electrons.
Figure 6. The observed position and isosurfaces of the molecular orbitals for Ag\textsubscript{14} and Ag\textsubscript{13}- with the color denoting the assigned subshell. Note that the 1F and 2P orbitals have been left out for clarity.

4. Conclusions
We have demonstrated that Ag\textsubscript{15}\textsuperscript{+} is resistant to reactivity with oxygen due to its large HOMO-LUMO gap, despite not having a magic number of electrons. The cluster is found to have a highly oblate structure, and the importance of this deformation is demonstrated by showing a correlation between an oblate deformation coefficient and the HOMO-LUMO gap of the different structures of Ag\textsubscript{15}\textsuperscript{+}. The unusually large HOMO-LUMO gap may be understood qualitatively as a crystal field like splitting of the jellium orbitals, in which the 1P\textsubscript{z}, 2S, D\textsubscript{xy} and D\textsubscript{x-y}\textsuperscript{2} orbitals are occupied as near frontier orbitals. An analysis of the molecular orbitals of Ag\textsubscript{15}\textsuperscript{+}, Ag\textsubscript{14} and Ag\textsubscript{13}- all reveal a similar electronic structure and a strongly oblate geometry. This work further demonstrates the interplay between the electronic structure and electronic structure and reveals how simple modifications of the spherical jellium model allow the intuitive understanding of cluster phenomenon. The present results also support our earlier finding that the s pin accommodation plays a determining role in the reactivity of silver clusters with oxygen.

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