CASSCF/Cl calculations of low-lying states and potential energy surfaces of Au₃

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Complete active space MCSCF (CASSCF) and second-order configuration interaction (SOCl) calculations of low-lying electronic states (2B₂, 2A₁) of Au₃ as well as the 1Σ⁺ state of Au₂ are carried out. The bonding potential energy surfaces of 2A₁ and 2B₂ states are also presented. A barrier is found in the potential energy surface of the 2A₁ state in moving from the linear to bent structure. Two nearly-degenerate structures are found for the ground state. The 2Σ⁺ state arising from the linear structure with an Au–Au bond length of 2.66 Å is only 3.2 kcal/mol below the 2A₁ bent state. The equilibrium geometry of the 2A₁ state is an isosceles triangle with an apex angle of 54°. The Au₃ cluster is found to be more stable than the gold dimer. The effect of d correlation is studied on Au₂ by carrying out MRSDCI (multireference singles and doubles CI) calculations on the 1Σ⁺ state of Au₂ which include excitations from the d orbitals.

I. INTRODUCTION

The investigation of the electronic structure and other properties of small metal clusters of heavy atoms is an interesting topic because it may provide information about metal–metal multiple bonding and about the transition from the molecular to the bulk state. Consequently, it is very useful to study such clusters as models in catalytic processes. There have been a few studies on the Au₃ cluster. 4–9 Theoretical investigation of Au₃ cluster is of fundamental interest since relativistic effects are quite large for these systems. Klotzbücher and Ozin 4 have observed an optical spectrum of absorption of Au₃ by the relaxed isolation method. However, they have not determined the electronic state assignment for Au₃ from the observed optical transitions although these authors have discussed tentative assignment of the spectra. Hilpert and Gingerich 5 have reported the average atomization energy deduced by thermodynamic third law from the experimental data of high temperature mass spectrum for Au₃: D₅(Au₃) = 3.81 eV for the linear geometry and Dₓ(Au₃) = 3.67 eV for the bent geometry. However, they have not yet directly answered which symmetry state is the ground state. Howard et al. 6,7 have recently published the first evidence of the existence of the gold neutral triatomic cluster by ESR spectroscopy of a bare gold cluster and pointed out that the ground state is 2B₂ state with an obtuse angle C₂v geometry structure.

Semi-empirical nonrelativistic calculations of Au₃ were carried out by Richtsmeier et al. 8,9 In these calculations, these authors used the semi-empirical diatomics in molecules (DIM) method and obtained an acute-angled triangular geometry (2B₁) for the ground state of Au₃. However, this geometry with an acute angle is contrasted with the experimental geometry of an obtuse angle.

Relativistic calculations of molecules containing very heavy atoms are a topic of considerable activity. 10–22 Balasubramanian and Pitzer 10 have recently reviewed the topic. From relativistic calculations of Au₂ carried out by a few authors 11–13 it has been shown that the other relativistic contributions are more important than the spin–orbit contribution for the ground state of Au₂. These calculations have also shown the electronic structure of Au₂ and Ag₂ from the same group 1B seems to be considerably different. Au₂ is found to be more stable than Ag₂. This anomaly is attributed to the relativistic contraction of the outer s of gold due to mass-velocity corrections. So far, ab initio calculations including relativistic corrections for Au₃ cluster have not reported.

In this investigation we present complete active space MCSCF (CASSCF) calculations followed by configuration interaction calculations (CI) on low-lying states of the Au₃ cluster to establish the ground state of Au₃ and the properties of other states. We also calculate the potential energy surfaces of two low-lying states of Au₃. Further, calculations on Au₃ which include high levels of d correlation are carried out with the objective of estimating the effect of d correlation on the stabilities and geometries of the larger clusters. In Sec. II, we describe the method of our investigation. Section III includes the results and discussion.

II. METHODS

The Au₃ cluster was oriented in the standard C₂v orientation with the x axis being perpendicular to the plane of the molecule. The low-lying electronic configurations of Au₃ in C₂v symmetry are,

1a¹ 2a¹
and
1a¹ 1b¹ 1b¹,

where we show only the MOs arising from the 6s atomic orbitals of the three Au atoms. In the D₃h symmetry (equilateral triangle), Au₃ has 2E' degenerate electronic state. This would be split apart into 2B₂ and 2A₁ components in the C₂v group as a result of the Jahn–Teller distortion. 23,24

We employ relativistic effective core potentials for the gold atom with the outer d 10s 1 shell included in the valence space. Ermier and Christiansen 22 have reported analytical
TABLE I. Valence basis sets of Gaussian-type functions for Au (3s3p3d / 3s2p3d).

<table>
<thead>
<tr>
<th>Shell</th>
<th>Exponential factor</th>
<th>Contract</th>
<th>coefficient</th>
</tr>
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<td>s</td>
<td>0.4409</td>
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<td></td>
</tr>
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<td>1.0</td>
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<tr>
<td></td>
<td>0.1664</td>
<td>1.0</td>
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Gaussian fits of these potentials which are useful in molecular calculations. We employ these potentials. These authors have also optimized a (3s3p3d) valence Gaussian basis set for the $^2S$ ground state of the Au atom. We contract the three $p$ functions into two $p$ functions with the contraction coefficients shown in Table I. The resulting basis set is of the type (3s2p3d).

The MCSCF calculations were carried out using the complete active space MCSCF (CASSCF) method. In this method, wave functions are constructed in the complete configuration space of strongly occupied orbitals of the separated atoms. For Au$_2$, the active space consisted of 2a$_g$ and 1b$_2$ orbitals which correlate into the 6s orbitals of the three gold atoms at infinite separation. The three outer electrons are distributed in all possible ways in the active space. The wave function obtained this way is labeled as CASSCF.

Configuration interaction (CI) calculations were carried out following CASSCF. The CI calculations carried out were second-order CI (SOCl) calculations. The SOCl calculations included (i) the configurations in the zeroth-order MCSCF, (ii) configurations generated by distributing two electrons in the MCSCF internal space and one electron in the orthogonal external space in all possible ways, and (iii) configurations generated by distributing one electron in the internal and two electrons in the external spaces in all possible ways. The effect of $d$ correlation is studied on Au$_2$ by carrying out MRSDCI (multireference singles and doubles CI) calculations which allow excitations from the $d$ shells. The CASSCF wave function of the $^1\Sigma^+$ ground state of Au$_2$ contains two configurations (coefficients $>0.03$), namely, 1$\sigma^2$ and 1$\sigma^2$. These two reference configurations were included in the MRSDCI together with the $d$ shell. Single and double excitations from these and the $d$ orbitals in the $A_1$ symmetry block were allowed in the MRSDCI calculations. Such MRSDCI calculations were not possible for Au$_3$ since the configuration space of such calculations span over a million configurations. The dimensions of the CASSCF and the CI spaces are shown in Table II. The calculations described here were carried out using one of the authors' modified version of ALCHEMY II package of codes to include relativistic effective core potentials.

### III. RESULTS AND DISCUSSION

Table III shows the optimized geometries and energies of low-lying electronic states of Au$_3$ and the $^1\Sigma^+$ ground state of Au$_2$ at equilibrium and long distance geometries as obtained by various methods. Figure 1 shows the bending potential energy surfaces of $^2A_1$ and $^2B_2$ states of Au$_3$. As one seen from Table III, we find two nearly-degenerate candidates for the ground state. The linear geometry ($^2\Sigma^+$) state is slightly more stable than the bent isosceles triangular ($^2A_1$) state. The Au–Au bond length of the $^2\Sigma^+$ state is 2.66 Å at the SOCl level. An additional shrinking of at least 0.05 Å is expected if $d$ correlation is included. Further, inclusion of $f$ functions in the basis set may shrink the Au–Au bond by about 0.02 Å. Thus, the actual Au–Au bond length

<table>
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<tr>
<th>System</th>
<th>State</th>
<th>Method</th>
<th>$r$ (Å)</th>
<th>$\theta$ (deg)</th>
<th>$E$ (hartrees)</th>
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<td>$^2B_1$(^1\Sigma^+)</td>
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<td>55.0</td>
<td>-99.971 36</td>
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<tr>
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<td>2.78</td>
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<td>$^4A_1$(^2\Sigma^+)</td>
<td>SOCl</td>
<td>2.75</td>
<td>180.0</td>
<td>-99.930 29</td>
</tr>
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<td>2.60</td>
<td>···</td>
<td>-66.647 37</td>
</tr>
<tr>
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<td>$^2\Sigma^+$</td>
<td>MRSDCI</td>
<td>2.56</td>
<td>···</td>
<td>-66.728 98</td>
</tr>
<tr>
<td>Au + Au</td>
<td>$^2\Sigma^+$</td>
<td>SOCl</td>
<td>7.50</td>
<td>···</td>
<td>-66.601 08</td>
</tr>
<tr>
<td>Au + Au</td>
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<td>7.50</td>
<td>···</td>
<td>-66.667 15</td>
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<tr>
<td>Au + Au</td>
<td>$^2\Sigma^+$</td>
<td>SOCl</td>
<td>7.50</td>
<td>···</td>
<td>-99.901 67</td>
</tr>
</tbody>
</table>

$r$ stands for the two equal distances of the isosceles triangle, for the linear structure it stands for the Au–Au bond length.
FIG. 1. Bending potential energy surfaces of the $^2A_1$ and $^2B_2$ states of Au$_3$. The Au–Au bond distances (equal sides of the triangle) were optimized for all bending angles.

of the $^2\Sigma^+_{g}$ state should be slightly less than 2.61 Å. The experimental assignment$^{6,7}$ of the ground state of Au$_3$ to the $^2B_2$ nearly-linear (obtuse triangle) structure is thus in agreement with our calculations. However, our results contrast with DIM calculations$^{8,9}$ which predict an acute-triangular structure for this state.

The optimized geometry of the $^2A_1$ state is an isosceles triangular structure with an apex angle of 55°. The apex angle is not very sensitive to higher order correlation corrections as seen from Table III. The $^2A_1$ isosceles triangular structure is only 3.2 kcal/mol above the linear ($^2\Sigma^+_{g}$) structure. Thus, it is conceivable that a calculation which uses a bigger basis set and includes higher-order correlation corrections may lower the isosceles triangular structure in comparison to the linear structure. Thus, we believe that both the structures (linear and isosceles triangle) are probable candidates for the ground state of Au$_3$.

We carried out calculations on the $^2\Sigma^+_{g}$ ground state of Au$_3$ with the objective of estimating the effect of d correlation on bond lengths and dissociation energies. The MRSDCI calculations which include excitations from all the d orbitals in the $A_1$ symmetry block yield a $D_1$ value of 1.68 eV and a Au–Au bond length of 2.56 Å. The corresponding SOCI $D_1$ value which does not include d correlation is 1.26 eV, thus indicating a correction of about 0.42 eV in $D_1$ or a d-correlation correction of about 0.21 eV/atom. Ross and Ermler$^{13}$ have obtained a $R_e$ value of 2.65 Å and a $D_1$ value of 1.58 eV for the $^2\Sigma^+_{g}$ state with a somewhat smaller CI scheme.

The atomization energy of Au$_3$ was calculated by disso-
ration is $1\sigma^2_{g} 2\sigma^2_{u}$. However, four configurations make substantial contributions to the $^2A_1$ state in the vicinity of the barrier ($\theta = 110^\circ$), which shows that correlation correction is large in this region. The $^2A_1$ state of the linear structure is dominated by the $1\sigma^2_{g} 1\sigma^2_{u}$ configuration, although the $1\sigma^2_{g} 2\sigma^2_{g}$ configuration also makes substantial contribution. Thus the barrier height in Fig. 1 at the CASSCF level would not be reliable since higher-order correlations can alter this height substantially.

Walch, Bauschlicher, and Langhoff\textsuperscript{27} have recently studied selected regions of potential energy surfaces of Ag$_3$, Cu$_3$, AuCu$_2$, and AgCu$_2$ trimers. SCF followed by SDCI calculations which include $d$ correlation yield a bent $^2B_2$ state for Ag$_3$ (apex angle = 69°).\textsuperscript{27} We attempted the same level of calculations described here for Au$_4$ on Ag$_3$. Such calculations yield a bent $^2B_2$ state but a somewhat larger apex angle than 69°. Thus, we are at present carrying out a CASSCF which include $d$ electrons in the active space for both Ag$_3$ and Au$_4$ with the intent of studying the effect of $d$ correlation on the apex angle of the $^2B_2$ state of Au$_4$. The results of these calculations on Ag$_3$ and Au$_4$ will be described in a future publication.

IV. CONCLUSION

In this investigation we carried out CASSCF/CI calculations of low-lying states of Au$_4$. CASSCF/SCF calculations predict that there are two nearly-degenerate structures for the ground state of Au$_4$. The $^2\Sigma^+_u$ linear structure (Au–Au bond length = 2.66 Å) is about 3.2 kcal/mol lower than the $^2A_1$ isosceles triangular structure (apex angle = 54°). The bending potential energy surfaces of the $^2B_2$ and $^2A_1$ were obtained. The Au$_4$ cluster is at least 1.0 eV more stable than the gold dimer.

ACKNOWLEDGMENT

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\textsuperscript{26} The major authors of ALCHEMY II codes are B. Liu, M. Yoshimine, and B. Langsfeld.