Infrared vibronic absorption spectrum and spin–orbit calculations of the upper spin–orbit component of the Au$_3$ ground state

Rui Guo  
Department of Applied Science, University of California Davis, L-794, Livermore, California 94550

K. Balasubramanian  
Department of Applied Science, College of Engineering, University of California Davis, Livermore, California 94550; Chemistry and Material Science Directorate, Lawrence Livermore National Laboratory, University of California, Livermore, California 94550 and Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Xuefeng Wang and Lester Andrews  
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319

(Received 18 January 2002; accepted 1 May 2002)

Laser-ablated gold co-deposited with excess neon at 3.5 K produces a new sharp 2025.5-cm$^{-1}$ absorption. Annealing to 8 K increases this absorption ten-fold and produces six weaker associated vibronic bands with 172- and 118-cm$^{-1}$ intervals. Relativistic configurations (RCI) computations are carried out for several electronic states lying below 4.4 eV. These calculations show that the spin–orbit effect stabilizes the $D_{3h}$ structure and quenches Jahn–Teller distortion. They also predict a 0.2-eV spin–orbit splitting of the Au$_3$ ground state, which is in excellent agreement with the 2025.5-cm$^{-1}$ neon matrix band origin. We have also confirmed the assignment of the A-X system at 1.8 eV observed by Bishea and Morse. The observed vibronic intervals are in accord with calculated $a'_1$ and $e'$ stretching fundamentals and they confirm the $D_{3h}$ geometry for Au$_3$. This work reports the first observation of the ground-state spin–orbit splitting of a heavy metal trimer. © 2002 American Institute of Physics. [DOI: 10.1063/1.1487815]

I. INTRODUCTION

Metal clusters are of considerable interest as they bridge the atomic and solid states. The homonuclear coinage metals are of particular interest because although bonding in the ground state arises from a single s electron on each atom, the metal d orbitals are involved in electron correlation and spin–orbit effects. The heavier trimers such as Au$_3$ are particularly interesting in that although the orbitally degenerate $2E'$ $D_{3h}$ ground state can undergo Jahn–Teller distortion to $2A_1$ and $2B_2$ states in $C_{3v}$ symmetry, spin–orbit splitting may be able to quench this distortion. This seems to be a consequence of the fact that the $2A_1$ and $2B_2$ states are degenerate at the $D_{3h}$ geometry, and thus spin–orbit mixing of these two states with opposite spins becomes large at the $D_{3h}$ geometry, thus resulting in larger spin–orbit stabilization than Jahn–Teller stabilization. When this happens the trimer does not undergo Jahn–Teller distortion and retains its ideal $D_{3h}$ geometry. Consequently, gold trimer is a very interesting candidate for the study of Jahn–Teller versus spin–orbit stabilization arising from the involvement of the 5d orbital of Au in bonding.

Early theoretical calculations for Au$_3$ employed the diatomics-in-molecules method and predicted a Jahn–Teller distortion from $D_{3h}$ to an isosceles triangular $B_2$ ground state with an apex angle $>60^\circ$. Later complete active space self-consistent field configuration interaction (CASSCF/CI) computations found two nearly degenerate [2$B_2$, 2$A_1$] structures for the ground state with the $2B_2$ state lower. The $2B_2$ state was lower than the $2A_1$ state in self-consistent field modified coupled pair functional (SCF-MCPF) calculations as well. A subsequent study has shown that spin–orbit interactions play an important role in the excited states of Au$_3$; hence spin–orbit effects must be included to understand the ground state. We show here the spin–orbit splitting is larger than the Jahn–Teller stabilization energy, and thus the spin–orbit coupling quenches the distortion resulting in $D_{3h}$ minima for the electronic states of Au$_3$.

The gold trimer was first observed by electron spin resonance in a C$_6$D$_6$ matrix and found to have unpaired spin population mostly on the terminal gold atoms. Optical absorptions of Au$_3$ were recorded at 292 and 471 nm in solid argon over 20 years ago using thermal evaporation as a gold-atom source. More recently mass-selected gold-cluster ions were neutralized and trapped in rare-gas matrices for observation of optical spectra in the same regions under more controlled experimental conditions. Even more recently, resonant two-photon ionization spectroscopy of jet-cooled Au$_3$ has located a new weak band system near 749 nm proposed to arise from a $4E' \rightarrow 2E'$ transition. It is noteworthy that this transition involves a 180-cm$^{-1}$ progression in the totally symmetric mode of the upper state, which allowed us to associate a 172-cm$^{-1}$ vibronic interval in the neon matrix infrared spectrum of gold clusters with Au$_3$. In recent investigations of laser-ablated gold-atom reactions with small molecules, we noticed a sharp 2025.5-cm$^{-1}$ absorption that increased with decreasing re-
agent concentration in the neon matrix. This unusual behavior suggested the possibility of a gold cluster and stimulated our interest. Accordingly, gold was co-deposited with pure neon, the absorbance increased markedly, and six additional weaker vibronic bands were observed. We report here the vibronic transition of spin–orbit components of the ground state Au$_3$ in solid neon and its theoretical interpretation. This represents the first observation of the ground-state spin–orbit components of a metal trimer.

We have also computed several electronic states of Au$_3$ lying below 4.4 eV employing CASSCF/multireference singles and doubles configuration-interaction (MRSDCI)/relativistic configuration-interaction (RCI) computations that included up to $5.2 \times 10^6$ configurations. The RCI calculations include electron correlation and spin–orbit effects variationally in a multireference configuration space constructed according to the double group of the molecule. Several upper roots of RCI computations were obtained and compared with current and other available experimental results. We have also made extensive double-group analysis of the electronic states and discuss the transitions in the double-group symmetry. The vibrational frequencies are computed and analyzed together with experimental results in the double group.

II. EXPERIMENT

The experimental methods for laser-ablation and matrix-infrared spectroscopy have been described previously. The Nd:Yttrium aluminum garnet (YAG) laser fundamental (1064 nm, 10 Hz repetition rate, 10-ns pulse width, 10–20 mJ/pulse) was focused onto a rotating gold-metall target. Neon was deposited on a cesium iodide window cooled to 3.5 K by a Sumitomo Heavy Industries RDK-205D cryocooler. Infrared spectra were recorded at 0.5-cm$^{-1}$ resolution on a Nicolet 750 spectrometer with 0.1-cm$^{-1}$ accuracy using a HgCdTe detector. Matrix samples were annealed at a range of temperatures and subjected to broadband irradiation by a mercury arc (Philips, 175 W) with the globe removed.

III. METHODS OF COMPUTATION

All of the computations were carried out with relativistic effective core potentials (RECPs) that retained the outer 5$d^{10}6$s$^1$ shells of the gold atom in the valence space, replacing the remaining electrons by RECPs. The basis sets compatible with these RECPs were taken from Ross et al. No contractions were made to the published 3$s^33$p$^4$d$^4$ valence Gaussian basis set. All calculations were performed in the $C_{2v}$ group and $C_{2v}$ double group.

Geometry optimizations of all the electronic states were done at the complete active space MCSCF (CASSCF) level. In all the calculations, 18 active orbitals originating from all of the 5$d$ and 6$s$ orbitals of gold atoms were included in the active space for the excited and ground electronic states uniformly. In the CASSCF calculations, all 33 electrons of Au$_3$ were distributed in all possible ways among the 18 active orbitals, which spanned seven $a_1$, five $b_2$, three $b_1$, and three $a_2$ orbitals in the $C_{2v}$ symmetry. This resulted in about 15 000 configuration spin functions (CSFs). The geometries of the electronic states of Au$_3$ were optimized in the same manner.

Our optimizations of the $^4A_1$, $^4B_1$, and $^4A_2$ states of the gold trimer in the CASSCF calculation lead to energy minima with bent geometries, while optimization of the $^4B_2$ state simply leads to three separate gold atoms, which indicates that this state is dissociative. The optimized geometries of the three stable quartet states, the $^2B_2$ ground state, and all electronic states computed before were considered. After energy minima were located at the CASSCF level, single-point calculations at the energy minima were done using the MRSDCI method to obtain more correlated relative energies by including higher-order correlation effects that are not included in the zeroth-order CASSCF. All configurations in the CASSCF with coefficient $\geq 0.07$ were included in the MRSDCI calculations, which includes up to $5.2 \times 10^6$ configurations for various states of Au$_3$. Subsequently, a multireference Davidson correction technique, labeled as MRSDCI+$Q$ in Table III, was invoked, which could be considered as estimates to the full CI limits.

A previous study has shown that the spin–orbit interaction plays an important role in the excited states of Au$_3$. The spin–orbit interaction was included using a multireference relativistic CI approach. In this method, all low-lying electronic states with the same symmetry in the $C_{2v}$ ($D_{3h}$) double group were included as reference configurations. Table I shows the list of reference configurations included in the RCI calculations made at the equilateral triangular geometry. The spin–orbit integrals are included variationally in a multireference CI scheme with the spin–orbit matrix elements built into the total Hamiltonian. The RCI calculations included up to 44 reference configurations arising from the electronic distributions shown in Table I, and a total of 90 874 configurations generated from single and double excitations of the reference configurations. All CASSCF geometry optimizations were made using GAMESS codes. The vibrational frequencies were calculated using the CASSCF method. All CASSCF/MRSDCI computations were made using one of the author’s modified version ALCHEMY II codes. The vibrational frequencies were computed using the GAMESS codes. The spin–orbit integrals using RECPs were computed using Pitzer’s ARGOS codes.

IV. RESULTS AND DISCUSSIONS

The infrared spectrum of a new gold cluster species is illustrated in Fig. 1. The strongest 2025.5-cm$^{-1}$ band was observed in laser-ablated gold experiments with O$_2$, NO, and CO in excess neon, and the band intensity increased with decreasing reagent concentrations and decreasing reagent reactivity. In experiments with H$_2$, the first three bands were observed. The illustrated spectrum in pure neon is 30 times stronger than the spectrum recorded with 5% H$_2$ in neon. This sharp band system appears to be due to a gold cluster.

The sharp 2025.5-cm$^{-1}$ absorption is weak on co-deposition of gold atoms in excess neon at 3.5 K, but annealing to 8 K to allow diffusion of trapped gold atoms increases...
the sharp 2025.5-cm\(^{-1}\) absorption ten-fold and produces six weaker associated absorptions. These seven sharp absorptions are virtually destroyed by broadband mercury arc (\(\lambda >240\) nm) irradiation. However, successive annealing to 10 K restores the seven bands with half again more intensity, and a final annealing to 12 K (not shown) decreases the bands by 50\% and produces a series of broad bands with similar intervals. The sharp band system is listed in Table II. A very weak, sharp 1212.6-cm\(^{-1}\) band (0.0005 absorbance units) produced on 12-K annealing is due to the AuOO absorption system. As in Fig. 1, subsequent annealing to 10 K restores the seven bands with half again more intensity, and a final annealing to 12 K (not shown) decreases the bands by 50\% and produces a series of broad bands with similar intervals. The sharp band system is listed in Table II. A very weak, sharp 1212.6-cm\(^{-1}\) band (0.0005 absorbance units) produced on 12-K annealing is due to the AuOO complex.\(^{11}\)

In a separate experiment, the sharp band system was produced by 7-K annealing after deposition. Exposure to \(\lambda >470\) nm radiation from the mercury arc reduced the sharp bands by 25\%, \(\lambda >380\) nm irradiation decreased the bands another 50\%, and \(\lambda >290\) nm photolysis destroyed the absorption system. As in Fig. 1, subsequent annealing (to 9 K) reproduced a stronger band system. It is clear that blue visible light dissociates the gold cluster and that it can be re-formed without activation energy. Hence, one of the states reached by absorption in the 3.0-eV region is dissociative.

Although the ground state of Au\(_3\) arises from the 5d\(^{10}\)6s\(^1\) shells of the gold atoms,\(^4\) the first excited state of the gold atom arises from an excitation of the 5d electron to the 6s orbital. The 5d\(^{10}\)6s\(^1\) configuration is \(\sim 4.9\) eV higher in energy and thus does not participate heavily in the low-lying excited states. This is in contrast with silver clusters for which the excited states arise from the promotion of 5s to 5p rather than from 4d to 5s. The low-lying excited electronic states of Au\(_3\) arise from excitation of electrons from the 5d orbitals to 6s orbitals of the gold atom. This is also clear from the reference configurations in Table I included in the RCI calculations, which shows that all the quartet states arise from an excitation from one doubly occupied orbital into two singly occupied orbitals relative to the leading \(^2B\(_2\)\) configuration. In contrast with smaller Ag clusters, whose excited states arise from an excitation of 5s to 5p orbitals, the 6s orbital of the gold atom is significantly stabilized by relativistic effects.

![Figure 1](image-url) **FIG. 1.** Infrared spectra in the 2800–2000-cm\(^{-1}\) region for Au\(_3\) (note different absorbance scales for 2800–2300 and 2400–2000 cm\(^{-1}\)). (a) Spectrum after co-deposition of laser-ablated gold in excess neon for 40 min, (b) after annealing to 8 K, (c) after broadband photolysis for 10 min, and (d) after annealing to 10 K.
Au$_3$ were found to lie above the 2 ground state, which the lowest 4 states presented earlier. It is also noted that the MRSDCI wave function and the double-group symmetry. As seen from Table IV, the ground-state spin–orbit splitting is 0.2 eV or about 1600 cm$^{-1}$.

The selection rules for the allowed spectroscopic transitions change in the $D_{3h}^2$ double group since spin and spatial symmetries are not good due to the spin–orbit coupling operator. The electronic transition between two double-group states is allowed if the direct product of the doubled-valued representations, in this case, contains the dipole operator. The dipole moment components transform as $A_1''$, $E'$, and $E''$ irrepertible representations in the double group. The direct products among the two two-valued irreducible representations of the double group, namely, $E_{1/2}$, $E_{3/2}$, and $E_{5/2}$ decompose into the following irreducible representations:

$$E_{1/2} \otimes E' = A_1'' \oplus E''$$

Thus the ground electronic state of Au$_3$ is split into $E_{1/2}$ and $E_{3/2}$ spin–orbit components. These are represented in Table IV by their leading $C_{2v}$ state contributor to the RCI wave function and the double-group symmetry. As seen from Table IV, the ground-state spin–orbit splitting is 0.2 eV or about 1600 cm$^{-1}$.

The selection rules for the allowed spectroscopic transitions change in the $D_{3h}^2$ double group since spin and spatial symmetries are not good due to the spin–orbit coupling operator. The electronic transition between two double-group states is allowed if the direct product of the doubled-valued representations, in this case, contains the dipole operator. The dipole moment components transform as $A_1''$, $E'$, and $E''$ irrepertible representations in the double group. The direct products among the two two-valued irreducible representations of the double group, namely, $E_{1/2}$, $E_{3/2}$, and $E_{5/2}$ decompose into the following irreducible representations:

$$E_{1/2} \otimes E_{1/2} = (A_1' \oplus A_2' \oplus E'')$$

$$E_{1/2} \otimes E_{3/2} = (E' \oplus E'')$$

$$E_{1/2} \otimes E_{5/2} = (A_1'' \oplus A_2'' \oplus E'')$$

The symmetric stretching mode is noted $a$, and doubly degenerate antisymmetric stretching mode is noted $e$.  

As shown in Table III, the three stable quartet states of Au$_3$ were found to lie above the 2$B_2$ ground state, among which the lowest 4$A_1$ state ($4E'$ in $D_{3h}$) is $\sim$1.8 eV higher. The 4$E'$ state is even lower than some of the excited doublet states presented earlier. It is also noted that the MRSDCI energy of 4$A_1$ is much lower than the CASSCF result, which indicates that a zeroth-order method like CASSCF is not adequate to describe the excited states of gold trimer properly.

The RCI calculations including spin–orbit coupling were made to extract up to 15 roots so that the electronic states can be computed including spin–orbit coupling. The weights of the leading configurations for most of the lower roots indicate significant spin–orbit mixing with states that would not mix in the absence of spin–orbit coupling, as shown in Table IV. The ultraviolet photoemission spectra of Au$_3$ obtained by Smalley and co-workers$^{21}$ were assigned to the various doublet states earlier by Balasubramanian and Das$^4$ with the lowest three states in Table III corresponding to peaks A, B, and C, respectively. According to our current study, the lowest quartet state, namely, 4$A_1$, will most likely overlap with some of the linear states. Our results of the vibrational frequencies for the states of interest are presented in Table V.

We have analyzed the electronic states of Au$_3$ in the double group and have suggested the assignment of the observed spectra on the basis of computed results. The Au$_3$ trimer is interesting in that even though the ground state predominantly arises from the 5$d^{10}6$s$^1$ electronic configuration, the spin–orbit splitting (0.2 eV) of the ground state of Au$_3$ is substantially larger than the Jahn–Teller stabilization energy of 0.06 eV as computed as the energy difference of the $D_{3h}$ structure and the $C_{2v}$ minimum at the MRSDCI level. Consequently, the Au$_3$ trimer retains its $D_{3h}$ symmetry, as the spin–orbit effect stabilizes the $D_{3h}$ structure, and quenches the Jahn–Teller distortion. Thus the assignment of the observed spectra and the discussion of the excited and ground electronic states should be considered in the $D_{3h}$ group with a planar triangular structure.

The inclusion of the spin–orbit coupling into the Hamiltonian changes the symmetry to the $D_{3h}^2$ double group for Au$_3$. The ground state in the absence of spin–orbit splitting is the 2$E'$ state, which would undergo pseudo-Jahn–Teller rotation$^{22–27}$ among the 2$B_2$ and 2$A_1$ states with $C_{2v}$ symmetry. However, the spin–orbit splitting is substantially larger than the barrier to pseudorotation. In the $D_{3h}^2$ double group, the doublet spin function correlates into the E$_{1/2}$ double-valued representation. The overall symmetries of the spin–orbit states of the ground state of Au$_3$ are obtained as the direct product:

$$E_{1/2}(\text{spin}) \otimes E' = E_{5/2} \oplus E_{3/2}.$$
TABLE IV. The RCI results of various Au$_3$ electronic states including spin–orbit coupling.

<table>
<thead>
<tr>
<th>State</th>
<th>Percentage composition</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^2$B$_1$(I)</td>
<td>$^2$B$_2$(3h$_2$): 58.2; $^2$A$_1$(4a$_1$): 33.8</td>
<td>0.00</td>
</tr>
<tr>
<td>$E^2$A$_1$(I)</td>
<td>$^2$A$_1$(4a$_1$): 58.5; $^2$B$_2$(3h$_2$): 33.9</td>
<td>0.2</td>
</tr>
<tr>
<td>$E^2$B$_1$(lin)</td>
<td>$^2$B$_2$ linear</td>
<td>0.7</td>
</tr>
<tr>
<td>$E^2$A$_1$(lin), $^2$B$_2$(III)lin, $^2$A$_2$lin</td>
<td>$^2$A$_1$(lin), $^2$B$_2$(II)lin, $^2$A$_2$lin, $^2$A$_1$(II)lin</td>
<td>1.3–1.6</td>
</tr>
<tr>
<td>$E^2$A$_1$(I)</td>
<td>$^4$A$_1$(4a$_1$2b$_2$3h$_2$): 62.7; $^4$B$_2$(2a$_1$4a$_1$3h$_2$): 15.4; $^4$B$_2$(3a$_1$4a$_1$3h$_2$): 4.4</td>
<td>1.8</td>
</tr>
<tr>
<td>$E^2$B$_2$(I)</td>
<td>$^4$B$_2$(2a$_1$4a$_1$3h$_2$): 43.1; $^4$B$_2$(3a$_1$4a$_1$3h$_2$): 39.4; $^2$B$_2$(4b$_2$): 4.5; $^2$A$_1$(4a$_1$2b$_2$3h$_2$): 2.6</td>
<td>3.0</td>
</tr>
<tr>
<td>$E^2$A$_1$(II)</td>
<td>$^2$A$_1$(6a$_1$): 44.7; $^2$A$_1$(2a$_1$), (3a$_1$): 29.8; $^2$B$_2$(4a$_1$3h$_2$): 2.6</td>
<td>3.4</td>
</tr>
<tr>
<td>$E^2$A$_1$(III)</td>
<td>$^2$A$_1$(5a$_1$): 62.0; $^2$A$_1$(2a$_1$), (3a$_1$): 16.9; $^2$A$_1$(4a$_1$2b$_2$3h$_2$): 5.1</td>
<td>3.6</td>
</tr>
<tr>
<td>$E^2$B$_2$(II)</td>
<td>$^4$B$_2$(2a$_1$4a$_1$3h$_2$): 25.7; $^4$B$_2$(3a$_1$4a$_1$3h$_2$): 18.8; $^2$A$_1$(4a$_1$2b$_2$3h$_2$): 18.6; $^2$B$_2$(4b$_2$): 11.3; $^2$A$_1$(6a$_1$), (2a$_1$), (3a$_1$), (5a$_1$): 5.9</td>
<td>4.0</td>
</tr>
<tr>
<td>$E^2$B$_2$(III)</td>
<td>$^2$B$_2$(3a$_1$4a$_1$3h$_2$): 42.8; $^2$B$_2$(4b$_2$): 30.4; $^2$B$_2$(2a$_1$4a$_1$3h$_2$): 7.8; $^2$A$_1$(6a$_1$), (5a$_1$): 2.5; $^2$A$_1$(4a$_1$2b$_2$3h$_2$): 2.4</td>
<td>4.0</td>
</tr>
<tr>
<td>$E^2$A$_1$(II)</td>
<td>$^4$B$_2$(2a$_1$4a$_1$3h$_2$): 31.0; $^4$B$_2$(3a$_1$4a$_1$3h$_2$): 23.3; $^4$B$_2$(1a$_1$4a$_1$3h$_2$): 5.7; $^4$A$_1$(4a$_1$2b$_2$3h$_2$): 8.4</td>
<td>4.3</td>
</tr>
<tr>
<td>$E^2$A$_1$(IV)</td>
<td>$^4$A$_1$(4a$_1$2b$_2$3h$_2$): 30.0; $^4$A$_1$(2a$_1$): 13.8; $^4$A$_1$(6a$_1$): 7.5; $^4$A$_1$(1a$_1$): 9.8; $^4$B$_2$(2a$_1$4a$_1$3h$_2$): 10.3; $^4$B$_2$(4b$_2$): 6.8</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Among the allowed transitions in the $D_{3h}^2$ double group, the lowest transition is the $E_{32}^2 ightarrow E_{52}^2$ transition, which is predicted to occur in the infrared region near 1600 cm$^{-1}$. A previous study$^{22}$ on Au$_2$ revealed a computed $B_0 u_+ - X_0 g^+$ energy separation of 28 828 cm$^{-1}$ including spin–orbit coupling compared to an experimental value of 25 686 cm$^{-1}$. Considering that this result is about 11% in error, the current result on Au$_3$ is in excellent agreement with the transition observed at 2025 cm$^{-1}$ in this study in view of the complexity of the RCI calculation. We believe that this is the first observation of the spin–orbit transition in the ground state of a heavy metal trimer. Note that the $^2B_2$ and $^2A_1$ Jahn–Teller $C_{2v}$ components of the ground state become the degenerate $^2E$ state in the $D_{3h}$ group. Therefore, the two states strongly interact due to spin–orbit coupling in the following manner. The $^2A_1$ state with open-shell spin function $\alpha$ couples to the $^2B_2$ state with spin $\beta$ though the following component of the spin–orbit operator, $L \cdot S$:

$$\langle m_\alpha | S_z | n_\beta \rangle$$

Since the two states are degenerate, the above spin–orbit matrix element is large enough to split the $E_{32}$ and $E_{52}$ components by 1600 cm$^{-1}$.

The $^4E'$ ($^4A_1$) excited state is of considerable interest, as this appears to have been observed by Bishea and Morse$^9$ using resonant two-photon ionization spectroscopy of jet-cooled Au$_3$. These authors observed a band with an origin located at 13 354 cm$^{-1}$, which extends over 700 cm$^{-1}$. On

---

TABLE V. Vibrational frequencies of Au$_3$ states.

<table>
<thead>
<tr>
<th>State</th>
<th>Vibrational frequencies (cm$^{-1}$)</th>
<th>Computed</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4B_1$</td>
<td>133.6 (2), 196.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4A_1$ ($^4E'$)</td>
<td>122.7 (2), 182.0</td>
<td>62, 180$^a$</td>
<td></td>
</tr>
<tr>
<td>$E^2A_1$</td>
<td>105 (2), 175</td>
<td>118, 172$^b$</td>
<td></td>
</tr>
<tr>
<td>$E^2B_2$</td>
<td>90 (2), 162</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$From Ref. 9.

$^b$From current work.
the basis of a relatively smaller oscillator strength, these authors have argued that among several possible considerations for the assignment of spectra, the most probable candidate is the $A^1E' \leftrightarrow X^1E'$ transition. As seen from Table IV, we indeed find a $E^1A_1$ state in the double group, which originates from the $4E'$ state in the absence of spin–orbit coupling. This state is computed at 1.8 eV above the ground state or a theoretically computed transition energy of 14500 cm$^{-1}$, which is in good agreement with the experimental value considering the complexity of electron correlation and spin–orbit effects for the excited electronic states of Au$_3$. The $4E'$ state actually correlates into the following direct product in the $D_{3h}^2$ double group:

$$E_{1/2}(\text{spin}) \otimes E' \otimes E_{3/2}(\text{spin}) \otimes E' = (E_{5/2} \otimes E_{3/2}) \otimes (E_{5/2} \otimes E_{1/2}) = (2E_{5/2} \otimes E_{3/2} \otimes E_{1/2}).$$

Therefore in the double group, the $4E'$ state gives rise to spin–orbit states to which transitions are allowed from the ground spin–orbit state. That is, from both $E_{5/2}$ and $E_{3/2}$ spin–orbit components, electronic transitions to all spin–orbit states of $A^1E'$ are dipole-allowed in the double group, although this transition is spin-forbidden in the normal point group.

As seen from Table V, we have computed the totally symmetric ($a'_1$) stretching frequency of the $4E'$ state as 182 cm$^{-1}$. Bishea and Morse$^9$ observed a vibrational progression in a totally symmetric stretching mode for this state with a frequency of 180 cm$^{-1}$, which is in excellent agreement with our 182 cm$^{-1}$ computed frequency. Bishea and Morse also fitted a much weaker progression in another mode to 62 cm$^{-1}$, but our second $e'$ stretching mode computed as 122.7 cm$^{-1}$ is somewhat higher than the interval for the weaker progression. We are not sure of the origin of this difference.

The six vibronic intervals built on the 2025.5 cm$^{-1}$ neon-matrix spin–orbit transition origin for Au$_3$ contain several pieces of information. First, the initial 172 cm$^{-1}$ interval appears four times. We expect the heavy-metal trimer Au$_3$ to have similar frequencies in the low-lying bound electronic states (that is, variations in frequencies may not be so dramatic due to three heavy atoms). Thus this band is analogous to the symmetric ($a'_1$) mode observed at 180 cm$^{-1}$ in the gaseous $E^1A_1$ state by Bishea and Morse$^9$ and further supports assignment of the neon matrix vibronic spectrum to Au$_3$. This may be compared to the 190 cm$^{-1}$ fundamental deduced for Au$_2$ from the electronic spectrum.$^{22}$ Our computed result for the Au$_2$ frequency is 193 cm$^{-1}$ for the ground state.$^{22}$ Second, notice that the third (2316.2 cm$^{-1}$) vibronic peak is stronger than the second (2198.0 cm$^{-1}$) peak: this pattern is repeated in the fifth (2488.2 cm$^{-1}$) and sixth (2601.5 cm$^{-1}$) peaks. These second intervals are 118 and 113 cm$^{-1}$, respectively. This interval corresponds to the antisymmetric ($e'$) stretching mode of Au$_3$ and it is analogous to the value computed for this mode in the $4B_1$ state (Table V). Thus the $a' + e$ combination peaks are about $\frac{4}{3}$ again stronger than the $a'$ peaks; this may arise in part due to double statistical weight for the degenerate vibrational state. Third, anharmonicity appears to play a greater role in higher combinations involving the antisymmetric stretching mode ($e'$) than the symmetric ($a'_1$) mode. Finally, the vibronic spectra are clean: only two modes are observed, the $a'_1$ and $e'$ modes, which show that the transition is correctly described by the double-group representation for the spin–orbit-split degenerate ground Au$_3$ state in $D_{3h}^2$ symmetry.

The vibronic selection rules under the $D_{3h}^2$ double group need to be considered for the specific spin–orbit states of Au$_3$. The total vibronic symmetry can be obtained as the direct product of the electronic symmetry in the $D_{3h}^2$ group and the symmetry of the vibrational modes. For the $e'$ vibrational mode the following direct products are obtained:

$$E_{3/2}(\text{electronic}) \otimes E'(\text{vibronic}) = (E_{5/2} \otimes E_{1/2}) (\text{vibronic}),$$

$$E_{3/2}(\text{electronic}) \otimes E'(\text{vibronic}) = (E_{3/2} \otimes E_{1/2}) (\text{vibronic}).$$

Thus, the $e'$ mode yields vibronic states to which transitions are allowed in the $D_{3h}^2$ double group, and it is readily seen that the symmetric stretch mode is active in the $D_{3h}^2$ double group. This further confirms the above assignment and an undistorted equilateral triangular structure for Au$_3$.

In the absence of spin-orbit coupling the $4E'$ state with $D_{3h}^2$ symmetry undergoes Jahn–Teller distortion by way of coupling with the $e'$ vibrational mode well known as the $E \otimes e$ Jahn–Teller coupling. The difference between the energy of the global distorted $C_{3v}$ ($2B_2$) minimum and the $D_{3h}^2$ cusp is the well-known Jahn–Teller stabilization energy. This is very small forAu$_3$ as evidenced from a very small distortion from the ideal $D_{3h}^2$ structure. On the other hand, the spin–orbit stabilization and the splitting into $E_{3/2}$ and $E_{5/2}$ spin–orbit components are much larger (0.2 eV) than the Jahn–Teller distortion. Thus the Au$_3$ trimer retains its $D_{3h}^2$ symmetry as confirmed by the observed spectra.

As indicated before, blue visible light dissociates the gold trimer. This is fully consistent with our computed $E^1B_2$ excited state of Au$_3$ at 3.0 eV (see Table IV), which is a dissociated state as it was found that the state is not bound. Consequently, the state reached by absorption in the 3.0-eV region is attributed to the $E^1B_2$ state computed to have a vertical energy separation of $\sim 3$ eV and is dissociative in nature.

V. CONCLUSIONS

Laser-ablated gold co-deposited with excess neon at 3.5 K produces a new sharp 2025.5 cm$^{-1}$ absorption. Annealing to 8 K increases this absorption ten-fold and produces six weaker associated vibronic bands with 172- and 118 cm$^{-1}$ intervals. RCI calculations show that the spin–orbit effect stabilizes the $D_{3h}^2$ structure and quenches Jahn–Teller distortion. Furthermore, RCI calculations predict a 0.2 eV spin–orbit splitting of the Au$_3$ ground state, which is in excellent agreement with the 2025.5 cm$^{-1}$ neon matrix band origin. The observed vibronic intervals are near calculated $a'_1$ and $e'$ stretching fundamentals and the clean progression in only $a'_1$ and $e'$ modes confirms the $D_{3h}$ geometry for Au$_3$ predicted.
by RCI calculations for Au$_3$. This work reports the first observation of the ground-state spin–orbit splitting of a heavy-metal trimer.

ACKNOWLEDGMENTS

The theoretical work at U.C. Davis was supported by the Office of Basic Energy Sciences, Chemical Sciences Division of U.S. Department of Energy under Grant No. DEFG02-86ER13558, and the work at LLNL was performed under the auspices of U.S. Department of Energy by University of California under Contract No. W-7405-Eng-48. The experimental work (Virginia) was supported by U.S. National Science Foundation Grant No. CHE00-78836.

19 R. M. Pitzer, ARGOS codes.