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COMMUNICATIONS

Is Au₆ a circular ring?

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I. INTRODUCTION

Taylor *et al.*¹ have recently reported the vibrational auto-detachment spectra of Au₆⁻. These authors found weakly-bound Au₆⁻ states for which the vibrational auto-detachment spectra were recorded. Such weakly-bound negative ion states especially for metal clusters are likely to be found since the extra electron is bound by image-charge forces as suggested by Taylor *et al.*

The remarkable feature of the observed vibrational spectra of Au₆⁻ is that only a single vibrational progression could be observed for a polyatomic cluster such as Au₆⁻. Based on this finding, Taylor *et al.*¹ suggested that the most attractive structure for Au₆ that is consistent with this spectrum is a D_{6h} gold ring analogous to benzene.

The spectroscopy of metal clusters in general and coinage metal clusters in particular is a very active area of study.¹⁻¹³ Theoretical calculations of these clusters are also on the increase.¹⁴⁻²²

In this investigation we carry out complete active space multiconfiguration self-consistent field (CAS-MCSCF) followed by multireference CI calculations on three possible candidates for the ground state structures of Au₆, namely, ¹A₁ with a capped-pentagonal structure (C_{5v}), ¹A_{1g} with a circular ring structure (D_{6h}) and an open-shell triplet state (³T_{2g}) with an octahedral structure. At all levels of theory considered here viz., CASMCSCF, second-order CI (SOCi) and multireference CI including d correlations (MRCI), the ¹A₁ state with capped pentagonal structure prevails. The corresponding calculations of Au₆⁻ reveal that at the lowest state with ring structure is the ²E_{2g} state. Hence, we reinterpret that the photodetachment spectra of Au₆⁻ at the ring geometry results in a ²E_{1u} excited state of Au₆⁻ which undergoes autodetachment to yield a metastable Au₆ neutral ring. The observed single vibrational progression is consistent with this structure although this is a local minimum and not a global minimum.

II. METHOD OF CALCULATIONS

In the CASMCSCF method, we retained all six valence electrons of Au₆ in the active space. The orbitals corresponding to the Au(5d) were allowed to relax but no excitations of electrons from these orbitals were allowed. The CASMCSCF active space comprised the 6s orbitals of

the separated Au atoms at infinite separation. We used the relativistic effective core potentials (RECPs) which retained outer 11 electron in the valence space. The basis sets and RECPs have already been described in detail in our previous study on Au₄.¹⁶

Three possible candidates (shown in Fig. 1) for the ground state of Au₆ were considered. The first structure which we call the capped pentagon (or a pentagonal pyramid) has an overall C_{5v} symmetry. It is made of five atoms forming a regular pentagon in a plane while the sixth atom is above the plane. The second structure is an Au₆ planar ring with D_{6h} symmetry. The ground state of the ring structure is ¹A_{1g}. The third structure considered here is of octahedral geometry but it has a triplet state as the lowest state. We restricted the present calculations to these three structures since these are the most attractive candidates that could explain Taylor *et al.*'s observed spectra.

The CASMCSCF/CI calculations of the capped pentagon were made in the C_s point group for convenience while the calculations of octahedral and ring structures were made in the D_{2h} group.

Following the CASMCSCF method, higher order correlations were included through the second-order configuration interaction (SOCi) method which correlated all six outer electrons and a restricted multireference configuration interaction (R-MRCI) method which correlated both d and s electrons.

The SOCi included (a) all configurations in the zeroth-order CASMCSCF, (b) those configuration generated by distributing five electrons in the CASSCF internal space and one electron in the external space in all possible ways, and (c) all configurations generated by distributing four electrons in the internal space and two electrons in the external space in all possible ways. At the SOCi level of theory, the remaining 60 electrons of Au₆ [predominantly Au(5d)] were kept in core.

The restricted multireference CI (R-MRCI) method included all configurations in the CASMCSCF with coefficients ≥ 0.1 as reference configurations. The most important 48 electrons of the Au₆ structure based on orbital eigenvalues were chosen and correlated. We allowed single and double excitations from these reference configurations

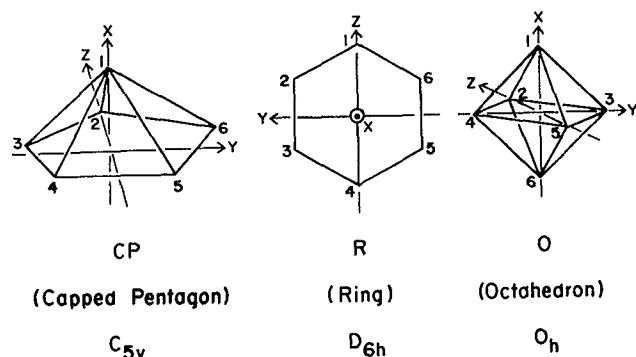


FIG. 1. Possible structures of Au_6 investigated in this study.

in the R-MRCI. To maintain consistency in the treatment of all three structures, we uniformly correlated 48 electrons. The external space was not truncated. But the possibility of two electrons in the external space was not allowed although for a single excitation in the external space, all single internal excitations were allowed. Even such an RMRCI resulted in a large configuration space. The above set of calculations was repeated for Au_6^- with three structures considered here. The bond lengths were optimized for each structure using a cubic polynomial fit.

The CASMCSF calculations made here included up to 95 configuration spin functions (CSFs) while the CI calculations included up to 435 300 CSFs. All calculations were done using one of the authors²³ modified version of ALCHEMY II codes²⁴ to include RECPs as described in Ref. 23.

III. RESULTS AND DISCUSSIONS

Table I shows our computed equilibrium geometries of the three structures shown in Fig. 1 at the CASSCF, SOCI, and R-MRCI levels of theory. As seen from Table I at all levels of theories, the capped pentagonal structure with 1A_1 symmetry is decisively lower than the alternative candidates viz., the Au_6 ring (D_{6h}) and an octahedral Au_6 structure.

As seen from Table I, the SOCI method which correlated the six outer electrons predicts the ring structure to

TABLE II. Geometries and energies of the Au_6^- clusters.

Structure	Symmetry	State	FOCI	
			R_e (Å)	E (eV)
R^b	D_{6h}	$^2E_{2g}$	2.713	0.0 ^a
O^b	O_h	$^2T_{1u}$	2.864	0.014
CP^b	C_{5v}	2E_2	2.773	0.331
			1.57	

^aZero energy for FOCI is $-200.025\,514$ a.u.

^b R_e s defined in footnotes e and f of Table I.

be 0.73 eV above the capped pentagon. The R-MRCI method which correlated 48 electrons places the Au_6 ring 1.4 eV above the capped pentagon while the octahedral structure is 1.5 eV above the capped pentagon. The Au–Au bond lengths in the three structures do not change substantially at various levels of theory.

We also investigated several excited states of Au_6 at the CASSCF level. For the ring structure, we found three excited states, namely, $^3B_{3g}$, $^1B_{3g}$ and 3A_g states. Their energy separations relative to the ground state are 2.76, 3.0, 2.76 eV, respectively. For the octahedral structure, however, the $^1T_{2g}$ excited state and a 1A_g state are only 0.2 and 0.5 eV above the ground state.

The FOCI results for Au_6^- are shown in Table II. We could not do SOCI or MRCI including d electrons due to too large a configuration space. The Au_6^- with ring structure was found to have the $^2E_{2g}$ state as the lowest, while the lowest state with the octahedral structure is $^2T_{1u}$. Although at the lowest level of theory (CASSCF), the octahedral structure is favored for Au_6^- , at the FOCI level of theory the ring structure prevails by 0.01 eV over the octahedral structure. It seems that further improvement in the basis set and inclusion of d electron correlation will favor the ring structure as the ground state of Au_6^- . A CI calculation which includes all 67 electrons of Au_6^- appears to be necessary to determine unequivocally the ground state of Au_6^- . The Au–Au bond length was found to be only 0.02 Å longer than the neutral bond length. The electron affinity of Au_6 is computed as 1.1 eV but the previous study on Au_4 (Ref. 25) reveals that the electron affinity obtained using *d*-correlated CI needs to be corrected by a scaling factor of 1.4 for basis set improvements and additional correlations.

TABLE I. Geometries and energies of the Au_6 clusters.

Structure	Symmetry	State	CASSCF		SOCI		R-MRCI	
			R_e (Å)	E (eV)	R_e (Å)	E (eV)	R_e (Å)	E (eV)
CP^d	C_{5v}	1A_1	2.77 ^e	0.0 ^a	2.81	0.0 ^b	2.77	0.0 ^c
			1.46 ^f		1.48 ^f		1.46 ^f	
R^d	D_{6h}	$^1A_{1g}$	2.70 ^e	1.01	2.72	0.73	2.66	1.39
O^d	O_h	$^3T_{2g}$	2.86 ^e	1.75	2.87	1.40	2.81	1.53

^aZero energy for CASSCF is $-200.001\,142$ a.u.

^bZero energy for SOCI is $-200.032\,428$ a.u.

^cZero energy for R-MRCI is $-200.085\,191$ a.u.

^dCapped pentagon, ring, octahedron (see Fig. 1).

^e $R_e = r_{1,2} = r_{1,3} = r_{1,4} = r_{1,5} = r_{1,6}$ for the CP; $R_e = r_{1,2} = r_{2,3} = r_{3,4} = r_{4,5} = r_{5,6} = r_{6,1}$ for the R; $R_e = r_{1,2} = r_{1,3} = r_{1,4} = r_{1,5} = r_{6,2} = r_{6,3} = r_{6,4} = r_{6,5} = r_{2,3} = r_{3,5} = r_{2,4} = r_{4,5}$ for the O.

^fOrigin-cap atom distance ($R_{0,1}$) for the CP.

Taylor *et al.*¹ did not find any excited state corresponding to Au₆ below 2.5 eV of the ground state. If Au₆ were to have octahedral structure, our calculations reveal that there are very low-lying excited states which are only 0.2–0.5 eV above the ground state. Since the experimental UPS spectra of Au₆[−] does not contain any peaks below 2.5 eV of the ground state peak, it seems that the octahedral structure is not an attractive candidate for the ground state of Au₆[−]. Furthermore, since the octahedral structure is considerably higher in energy, two possible candidates for the ground state of Au₆ may be considered. At all levels of theory considered here, the capped pentagon is favored.

Taylor *et al.*¹ argue that because they see only a single vibrational progression for Au₆ in the detachment spectra of Au₆[−] the ground state of the neutral structure must be a symmetric ring. Taylor *et al.* argue that there are only two possible structures with symmetries that lead to only a single vibrational progression. These are the symmetric ring structure and the octahedral structure. Taylor *et al.*'s extended Huckel calculations showed that the octahedral structure has an open-shell ground state consistent with our finding. They ruled out the octahedral structure based on the EH lowest unoccupied molecular orbital–highest occupied molecular orbital gap. The ring structure was considered the most attractive candidate for the ground state of Au₆ which gives a single vibrational mode (symmetrical breathing mode).

The capped pentagonal structure (see Fig. 1) has two possible symmetric vibrational modes. The one is the breathing motion of the ring while the other mode corresponds to the up and down motion of the capped gold atom. We computed the vibrational frequency for the up and down motion as 100 cm^{−1} by a cubic polynomial fit for the potential energy surface for this degree of freedom assuming that this motion is not strongly coupled to the breathing motion. The frequency of the breathing motion should be at least comparable since for the Au₆[−] ring (breathing motion) Taylor *et al.* obtain a frequency of roughly 108 cm^{−1}. Hence, if the autodetachment of the excited state of Au₆[−] led to the neutral Au₆ with the capped structure, two vibrational progressions should have been observed.

All above arguments lead to a possible reinterpretation of the observed spectra. In Taylor *et al.*'s experiment it seems that Au₆[−] ion in a ²E_{2g} state with a ring structure is first excited to a ²E_{1u} excited state of Au₆[−]. The autodetachment of an electron from this state results in a neutral ¹A_{1g} state of Au₆ with the ring structure. Since the ²E_{1u} excited state of Au₆[−] is formed from a vertical excitation of the ²E_{2g} state, detachment of electron from ²E_{1u} favors the ring structure of Au₆. The ring structure is certainly a local minimum in the potential energy surface although this is not the global minimum as seen from Table I. This seems to be the most consistent interpretation with the results of our calculations and the ultraviolet photoemission spectroscopy spectra of Taylor *et al.*

Our previous calculations^{15,16} on Au₄, Ag₄ and Cu₄ tetramers have revealed remarkable resemblance of these clusters to alkali metal tetramer structures. All three coin-

TABLE III. Leading configuration in the CI wave functions for the three structures of the Au₆ cluster.

Structure	Symmetry	State	Configuration	Weight
CP	C _{5v}	¹ A ₁	1a ₁ ² 1e ₁ ⁴	90%
R	D _{6h}	¹ A _{1g}	1a _{1g} ² 1e _{1u} ⁴	87%
O	O _h	³ T _{2g}	1a _{1g} ² 1t _{1u} ⁴	91%

age metal tetramers have ¹A_g ground states with rhombus geometries akin to alkali metal tetramers.²⁶ Consequently, the ground state structures of group IB clusters exhibit close similarity to the alkali metal clusters since the bonding in group IB clusters arises primarily from the outer valence *ns* orbitals although *d* electron correlation effects are important. Koutecky *et al.*¹⁴ find the ground state structure of Li₆ to be capped pentagonal. The Na₆ cluster also has the same structure.²⁷ The recent calculations of Koutecky *et al.*²⁸ also support our finding that the neutral and anions of these clusters have different structures.

Taylor *et al.* concluded that extensive 5*d*–6*s* hybridization would be sufficient to make the ring structure of Au₆ more stable relative to the capped pentagon. While there is some mixing of some of the Au(5*dxz*) orbital with 6*s* in the active orbitals of Au₆, our calculations reveal that there is not substantial mixing between 5*d* and 6*s* to make a stable ring structure for neutral Au₆.

Table III shows the leading configurations contributing to various states of Au₆. We find that for all three structures the leading configuration dominates (> 87%). As seen from Table III, the leading configuration of Au₆ is 1a₁²1e₁⁴ in the capped pentagonal structure. Thus Au₆[−] with CP structure has a 1a₁²1e₁⁴1e₂² configuration with a ²E₂ state. Hence it will undergo Jahn–Teller distortion. The leading configuration of the ring structure (1a_{1g}²1e_{1u}⁴) is very similar to the CP structure. The Au₆[−] with ring structure has 1a_{1g}²1e_{1u}⁴1e_{2g}² configuration. The leading configuration of the octahedral structure is 1a_{1g}²1t_{1u}⁴ which yields a ³T_{2g} state for Au₆. Hence the octahedral-structure will undergo Jahn–Teller distortion. But previous studies on Au₃ (Ref. 17) reveal that the Jahn–Teller stabilization energy is rather small. In any case it is unlikely to be of the order of 1.4–1.8 eV to make the distorted octahedral structure the ground state of Au₆.

IV. CONCLUSION

Our CASSCF/CI calculations reveal that Au₆ has a ¹A₁ ground state with capped pentagonal symmetry (C_{5v}). The ring and octahedral structures are found to be 1.4 and 1.5 eV, respectively, above the capped pentagon. We conclude that the photodetachment spectra of Au₆[−] from a image-charge-bound ²E_{1u} excited state with a D_{6h} ring structure results in a neutral Au₆ in a metastable ring structure which is however, not a global minimum for Au₆.

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- ¹K. J. Tylor, C. Jin, J. Conceicao, L. S. Wang, D. Cheshnovsky, B. R. Johnson, P. J. Nordlander, and R. E. Smalley, *J. Chem. Phys.* **93**, 7515 (1990).
- ²V. Bonačić-Koutecký, M. M. Kappes, P. Fantucci, and J. Koutecký, *Chem. Phys. Lett.* **170**, 26 (1990).
- ³K. Balasubramanian, *J. Mol. Structure (THEOCHEM)* **202**, 291 (1989).
- ⁴M. D. Morse, *Chem. Rev.* **86**, 1049 (1986).
- ⁵W. Weltner, Jr. and R. J. Van Zee, *Annu. Rev. Phys. Chem.* **35**, 291 (1984).
- ⁶E. A. Rohlfing and J. J. Valentine, *J. Chem. Phys.* **84**, 6560 (1980).
- ⁷M. Moskovits and J. E. Hulse, *J. Chem. Phys.* **67**, 4271 (1977).
- ⁸D. E. Powers, S. G. Hansen, M. E. Geusic, D. L. Michalopoulos, and R. E. Smalley, *J. Chem. Phys.* **78**, 2866 (1983).
- ⁹D. Cheshnovsky, C. L. Pettiette, and R. E. Smalley, *UPS of Metal and Semiconductor Clusters, Ion and Cluster Ion Spectroscopy*, edited by J. P. Maier (Elsevier, Amsterdam, 1988).
- ¹⁰M. F. Jarrold and K. M. Creegan, *Chem. Phys. Lett.* **166**, 116 (1990).
- ¹¹P. Y. Cheng and M. Duncan, *Chem. Phys. Lett.* **152**, 341 (1988).
- ¹²W. E. Klotzbücher and G. A. Ozin, *Inorg. Chem.* **19**, 3767 (1980).
- ¹³C. L. Pettiette, S. H. Yang, M. J. Craycraft, J. Conceicao, R. T. Laaksonen, O. Cheshnovsky, and R. E. Smalley, *J. Chem. Phys.* **88**, 5377 (1988).
- ¹⁴J. Koutecký, I. Boystanti, and V. Bonačić-Koutecký, *International J. Quantum Chem.* **38**, 149 (1990).
- ¹⁵K. Balasubramanian and P. Y. Feng, *J. Phys. Chem.* **94**, 1536 (1990).
- ¹⁶K. Balasubramanian, P. Y. Feng, and M. Z. Liao, *J. Chem. Phys.* **91**, 3561 (1989).
- ¹⁷K. Balasubramanian and M. Z. Liao, *Chem. Phys.* **127**, 313 (1988).
- ¹⁸K. Balasubramanian and P. Y. Feng, *Chem. Phys. Lett.* **159**, 452 (1989).
- ¹⁹K. Balasubramanian, *J. Phys. Chem.* **93**, 6585 (1989).
- ²⁰R. B. Ross and W. C. Ermler, *J. Phys. Chem.* **89**, 5202 (1985).
- ²¹K. Raghavachari and C. M. Rohlfing, *J. Chem. Phys.* **89**, 2219 (1988).
- ²²J. Flad, G. Igel-Mann, H. Preuss, and H. Stoll, *Chem. Phys.* **90**, 257 (1984).
- ²³K. Balasubramanian, *Chem. Phys. Lett.* **127**, 585 (1986).
- ²⁴The major authors of *ALCHEMY II* are B. Liu, B. Lengsfeld, and M. Yoshimine.
- ²⁵K. Balasubramanian and K. K. Das, *Chem. Phys. Lett.* (in press).
- ²⁶F. Spieglmann and D. Pavolini, *J. Chem. Phys.* **89**, 4954 (1988).
- ²⁷Y. Wang, T. F. George, D. M. Lindsay, and A. C. Beri, *J. Chem. Phys.* **86**, 3493 (1987).
- ²⁸V. Bonačić-Koutecký, P. Fantucci, and J. Koutecký, *J. Chem. Phys.* **93**, 3802 (1990).