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Experimental and Theoretical Investigation of the Electronic and Geometrical Structures of the Au₃₂ Cluster**

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Gold clusters and nanoparticles have received significant attention in cluster science because of their potential applications in nanotechnology.^[1–4] The discovery of unexpected catalytic properties of nanosized gold particles supported on substrates^[5] has rekindled extensive interest in the chemical and physical properties of gold clusters. The strong relativistic effects of gold^[6] results in Au clusters exhibiting many unique properties that are different from the other coinage metals. For example, gold clusters assume two-dimensional (2D) structures even at relatively large sizes, whereas the corresponding Cu and Ag clusters are three-dimensional (3D).^[7,8] The most recent surprise in Au cluster chemistry is the prediction of a highly stable Au₃₂ cage cluster,^[9,10] which was calculated to have the same icosahedral (*I_h*) symmetry as C₆₀ and can be regarded as having one atom located on each of

the 32 faces of C₆₀. Such a high symmetry structure with a hollow core is intriguing, but completely unexpected for a metal cluster. Explanations involving aromaticity and the tendency of Au to form 2D structures have been proposed to account for the stability of this unusual cluster.^[9,10] Should such a Au₃₂ cage be stable enough to be synthesized, it is anticipated to possess some fascinating physical and chemical properties. However, this structure has not been confirmed experimentally and it is not known how stable this structure would be in a charged state or upon ligand coordination. The stability towards ligand coordination will be particularly important if bulk quantities of Au₃₂ are to be made.^[11]

Although the direct experimental determination of cluster structures has been challenging, electron diffraction studies of trapped ions have recently shown considerable promise.^[12] Photoelectron spectroscopy (PES) of size-selected anions in combination with quantum-mechanical calculations has been shown to be a powerful indirect approach to yield structural information for clusters.^[13–15] By using this approach, we recently discovered that Au₂₀ possesses a highly symmetric and compact structure,^[16] which has since been confirmed in numerous studies to be the global minimum of Au₂₀.^[17–19] Herein, we describe the combination of PES and density functional theory (DFT) calculations to elucidate the electronic and geometrical structures of Au₃₂ and Au₃₂[−].

The experiment was performed by using a laser vaporization magnetic-bottle PES apparatus^[20] similar to that used in our previous studies on Au₂₀[−].^[16] The anionic Au₃₂[−] clusters were produced by laser vaporization of a gold foil and their mass was analyzed by means of time-of-flight mass spectrometry. PES spectra of Au₃₂[−] (Figure 1) were measured at two

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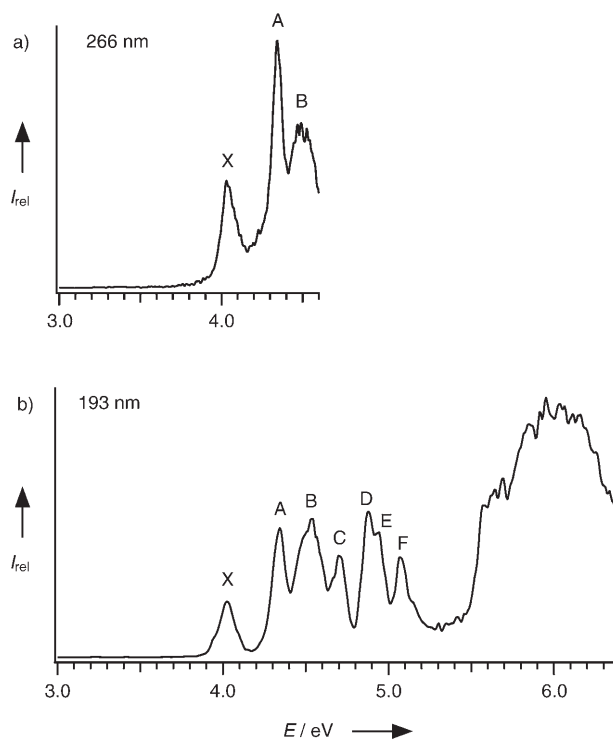


Figure 1. Photoelectron spectra of Au₃₂[−] at a) 266 nm (4.661 eV) and b) 193 nm (6.424 eV).

photon energies (266 nm (4.661 eV) and 193 nm (6.424 eV)) at an electron kinetic energy resolution of $\Delta E_k/E_k \approx 2.5\%$ (ca. 25 meV for 1-eV electrons). The general spectral pattern in Figure 1 agrees with a previous PES study of the coinage metal clusters,^[21] but considerable fine features were resolved in the current spectra in the lower-binding-energy range: a total of seven discrete bands were resolved (labeled as X, A–F). The higher-binding-energy range (>5.5 eV) exhibited continuous spectral features derived from the Au 5d band. The discrete, lower-binding-energy features were ascribed primarily to the Au 6s states and should be very sensitive to the structure of the cluster. The well-resolved bands in this spectral range make it possible to compare the results with theoretical calculations. The X band revealed the electron affinity of Au₃₂ to be 3.96 ± 0.02 eV. The PES spectral pattern indicates that Au₃₂ has a closed-shell electronic structure with a relatively small energy gap of 0.30 eV, defined by the X–A separation (Figure 1). It should also be pointed out that the observed main spectral features (X, A–F) were not dependent on the source conditions, which suggests that higher-energy isomers were not present in the beam in significant amounts.

Our calculations are based on plane-wave and Slater-basis DFT with the generalized gradient approximation (GGA) as implemented in the VASP^[22] and ADF^[23] codes.^[24] Our previous theoretical search showed that for neutral Au₃₂, the *I_h* cage is the most stable structure with the nearest-energy isomer (*D_{6h}*) 0.94 eV higher in energy.^[10] We found that the *I_h* cluster with a slight Jahn–Teller distortion (*D_{3d}*) remains the lowest energy structure for Au₃₂[−] (Figure 2 a and Table 1), but the closest-energy noncage isomer (*C₁-I*; Figure 2 b) is only 0.40 eV higher in energy on the basis of the ADF calculations. Four other low-lying isomers of Au₃₂[−] are also shown in Figure 2. Table 1 gives the electron configuration, relative energy, adiabatic detachment energy (ADE), and vertical detachment energy (VDE) for the six isomers of Au₃₂[−], as well as the electron configurations and the energy gaps for the corresponding neutral Au₃₂ isomers. The Jahn–Teller effect meant that several lower-symmetry species had to be considered for the cage structure of Au₃₂[−]. The structural distortions are all very minor and the four lower-symmetry structures are close in energy (Table 1). With the exception of the planar (*C_{2v}*) structure, the other low-lying isomers (*C₁-I*, *D_{6h}*, *C₂*, and *C₁-II*) of Au₃₂[−] are also close in energy. The two *C₁* isomers have no symmetry elements and can be characterized as being amorphous. These two structures and the *C₂* isomer are three dimensional, whereas the *I_h* and *D_{6h}* structures are cages, which can be considered to be quasi-2D because they are hollow. The three low-symmetry 3D structures are more compact and can be regarded essentially as distorted cages with two to four atoms inside.

The *I_h* Au₃₂ cluster has been shown to possess a very large

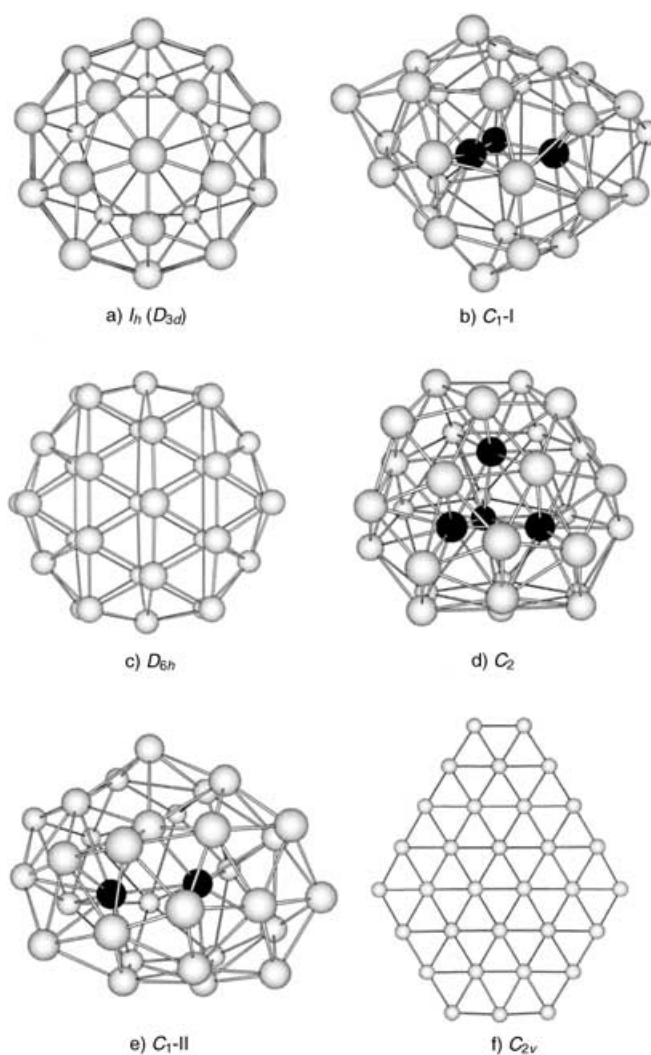


Figure 2. Selected structures of the Au₃₂[−] cluster: a) the global minimum icosahedral cage structure, b) first isomer with *C₁* symmetry (*C₁-I*), c) isomer with *D_{6h}* symmetry, d) isomer with *C₂* symmetry, e) second isomer with *C₁* symmetry (*C₁-II*), f) planar structure with *C_{2v}* symmetry.

Table 1: Optimized structures and electron configurations for Au₃₂ and Au₃₂[−], HOMO–LUMO energy gaps (ΔE_{HL}) for Au₃₂, relative total energies [$\Delta E(\text{tot})$], and adiabatic (ADE) and vertical (VDE) detachment energies for Au₃₂[−], all calculated by the ADF PW91/TZ2P method.^[a]

neutral			anion				
Sym.	Config.	ΔE_{HL}	Sym.	Config.	$\Delta E(\text{tot})$	ADE	VDE
<i>C_{2v}</i>	(b ₂) ² (a ₁) ⁰	≈0	<i>C_{2v}</i>	(b ₂) ² (a ₁) ¹	2.50	4.28	4.32
<i>C₁</i>	(a) ² (a) ⁰	0.44	<i>C₁-II</i>	(a) ² (a) ¹	0.81	3.74	3.79
<i>C₂</i>	(b) ² (a) ⁰	0.39	<i>C₂</i>	(b) ² (a) ¹	0.46	3.94	4.11
<i>D_{6h}</i>	(e _{1u}) ⁴ (e _{2g}) ⁰	0.84	<i>D_{2h}</i> ^[b]	(b _{3u}) ² (b _{1g}) ¹	0.41	3.63	3.68
<i>C₁</i>	(a) ² (a) ⁰	0.22	<i>C₁-I</i>	(a) ² (a) ¹	0.40	3.96	4.03
<i>I_h</i>	(g _u) ⁸ (g _g) ⁰	1.56	<i>D_{5d}</i>	(e _{2u}) ⁴ (a _{1g}) ¹	0.16	2.90	3.02
			<i>D_{2h}</i>	(a _{1u}) ² (a _{1g}) ¹	0.02	3.05	3.10
			<i>C_{2h}</i>	(b _u) ² (b _g) ¹	0.01	3.06	3.16
			<i>D_{3d}</i>	(a _{1u}) ² (a _{1g}) ¹	0.00	3.06	3.15

[a] All energies are in eV. The HOMO–LUMO energy gaps are for the optimized neutral species. [b] The structural distortion in the anion is very small and the anion symmetry is very close to the neutral *D_{6h}* structure.

HOMO–LUMO gap because of its high symmetry. Energy gaps of 1.7 and 2.5 eV were evaluated from the BP86 and PBE0 functions, respectively,^[9] whereas an energy gap of 1.5 eV was given by using the VASP code.^[10] These values are considerably larger than the 0.30 eV measured in our PES spectra of Au_{32}^- , which suggests that the experimentally observed Au_{32}^- cannot be the I_h cluster. To help determine the structure of Au_{32}^- , we computed the ADE and VDE of all the six low-lying isomers for comparison with the experimental PES spectra. As shown in Table 1, the calculated ADEs for the C_{1-I} isomer (3.96 eV) and the C_2 isomer (3.94 eV) are both in agreement with the experimental value (3.96 ± 0.02 eV), whereas that of the I_h structure is considerably smaller. The calculated ADEs of the other isomers are also in poor agreement with the experimental value. The computed VDE spectra, convoluted with Gaussian-shaped bands (0.05 eV full width at half-maximum (fwhm)) to approximately simulate the PES spectra,^[16] are shown in Figure 3

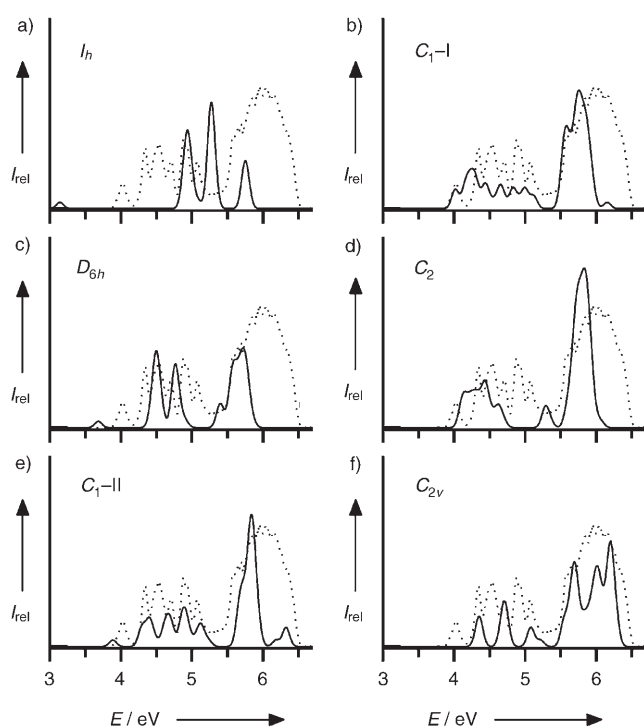


Figure 3. Simulated photoelectron spectra for the different isomers of Au_{32}^- overlaid with the experimental spectrum at 193 nm (dotted curves): a) the icosahedral cage structure, b) the C_{1-I} structure, c) the D_{6h} structure, d) the C_2 structure, e) the C_{1-II} structure, f) the planar C_{2v} structure. The simulated spectra were constructed by fitting each of the vertical detachment transitions with a Gaussian of 0.05 eV width.^[16]

overlaid with the experimental PES spectrum at 193 nm. The simulated spectrum of the I_h isomer (Figure 3 a) is very simple as a result of its large HOMO–LUMO gap caused by the high symmetry of this cage structure. The simulated spectra of the D_{6h} and the C_{2v} planar structures are also quite simple because of their relatively high symmetries. These spectra clearly disagree with the experimental PES data (Figure 3 c and f).

The simulated spectra of the three low-symmetry structures display some similarities (Figure 3 b, d, e): all have an intense band above 5.5 eV derived from the high density of states of the 5d electrons. However, the lower-binding-energy parts of the simulated spectra are highly structured and exhibit clear differences, which seem to be quite sensitive to the detailed structure of the clusters. The simulated spectrum of the C_2 structure (Figure 3 d) is very congested near the threshold region between 4.0 and 4.8 eV, which is followed by a gap and another band at 5.3 eV. This simulated pattern is clearly inconsistent with the observed PES spectra shown in Figure 1. At first glance, the simulated spectrum of the C_{1-II} structure (Figure 3 e) seemed to display some similarity to the experimental spectra. However, the calculated ADE for the first peak of this structure (3.74 eV) is considerably smaller than the experimental value (3.93 eV). The number of bands between 4.2 and 5.1 eV is also inconsistent with the experimentally observed bands. Furthermore, the total energy of the C_{1-II} structure is 0.81 eV higher than the ground state, which means that this structure is unlikely to be present under our experimental conditions (see below). On the other hand, the calculated ADE of the C_{1-I} structure (3.96 eV) is in excellent agreement with the experimental data (3.96 ± 0.02 eV), so that the first peak of the simulated spectrum of the C_{1-I} structure (Figure 3 b) coincides with the first experimental peak. The calculated HOMO–LUMO gap (0.22 eV) for the C_{1-I} structure seems to be slightly smaller than the measured gap of 0.3 eV. The number of bands and their positions in the low-binding-energy part of Figure 3 b (except the HOMO–LUMO gap) are in excellent agreement with the observed PES spectra for Au_{32}^- . Overall, the simulated spectrum of the C_{1-I} structure agrees best with the PES spectra.

Although the C_{1-I} isomer lies closest in energy above the I_h structure on the basis of our DFT calculations, it is still 0.4 eV higher. Why was this isomer observed experimentally, whereas the energetically more favorable Au_{32}^- cage was not? To understand this apparent paradox, we considered the relative stabilities of the various isomers as a function of temperature by taking into account the contribution of entropy, that is, by considering the free energy. We calculated the free energies of all of the six low-lying structures of Au_{32}^- by using the calculated total binding energies (E_0) from ADF at zero temperature and the harmonic vibrational entropy with Equation (1).^[25]

$$F = E_0 - \frac{1}{2} \sum_i \hbar \omega_i + k_B T \sum_i \ln \left(\exp \frac{\hbar \omega_i}{k_B T} - 1 \right) \quad (1)$$

In this equation, F is the free energy, E_0 is the total binding energy calculated with ADF, and the last two terms give the vibrational entropic contribution to the free energy at finite temperature by using the harmonic approximation and summing over all the vibrational degrees of freedom ($3n-6=90$ for Au_{32}^-). Figure 4 shows the computed curves for the free-energy of the six low-lying structures of Au_{32}^- relative to that of the D_{3d} cage structure as a function of temperature. We found that although the I_h cage is the most stable structure at zero temperature, the relative stability of

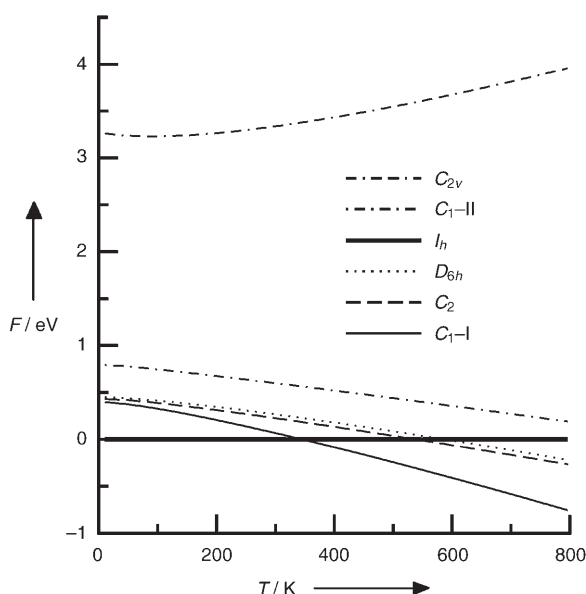


Figure 4. Free energies of the six low-lying isomers of the Au_{32}^- cluster as a function of temperature, calculated using a harmonic approximation and the ADF total binding energy at zero temperature. The free energies are plotted relative to that of the D_{3d} cage structure to show more clearly that several low-symmetry isomers become more stable at high temperatures as a result of the entropic effect. Note that the C_{1-I} structure becomes the most stable isomer at temperatures $> \approx 300$ K.

the C_{1-I} isomer increases rapidly with temperature because of the contributions from vibrational entropy. Significantly, we observed that the C_{1-I} isomer becomes the most stable cluster above approximately 300 K. Although the actual cluster temperature in our experiment was not known, our previous experience shows that for medium-sized Al clusters, a vibrational temperature of room temperature or slightly lower can be achieved.^[26] The large size of the Au_{32}^- cluster and the ineffectiveness of the supersonic cooling means our best estimate for its vibrational temperature even under our relatively cold source conditions is that it was probably around or slightly below room temperature. Considering the approximate nature of the free-energy calculations, we conclude that the formation of the amorphous C_{1-I} Au_{32}^- cluster in our experiment was indeed controlled by the vibrational entropy. It should be pointed out that the C_{1-II} isomer is higher in energy than the lowest-energy C_{1-I} isomer at room temperature by 0.5 eV, which makes it very unlikely that it is significantly formed under our experimental conditions. This view is reinforced by the observation that the C_2 and D_{6h} isomers, which are both more stable than the C_{1-II} isomer, do not seem to have any contribution to the observed spectra. Furthermore, aurophilic interactions,^[6] which may not be completely accounted for in the DFT calculations, are expected to favor the 3D structures, which would bring the energy of the C_{1-I} structure even closer to the cage structure. All these observations lend credence to our assignment that the C_{1-I} structure is the dominant cluster observed in our experiment.

In a similar recent study on the B_{20}^- cluster, we found that although a 3D ring-type structure was predicted by DFT

calculations to be the global minimum, only planar structures were observed experimentally because of the large entropy contributions of the planar structures at finite temperatures.^[27] This recent study along with the current work suggest that vibrational entropies are important in controlling the stabilities of relatively large cluster structures when isomers are closely lying in energy. Thermal effects have to be considered when comparing experiments performed at finite temperatures with theoretical calculations.

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length of the Au dimer and the lattice constant of the crystalline solid. The values obtained are in agreement with experimental data to within 2%. To facilitate comparisons with the experimental results, we carried out an extensive search for the global minimum of Au_{32}^- by simulated annealing, starting with various structures previously found for neutral Au_{32} ,^[10] as well as many other low-symmetry structures. The atomic structures were optimized by the conjugated-gradient method with a force convergence of $1.0 \times 10^{-3} \text{ eV \AA}^{-1}$.

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