Trianionic gold clusters

C. Yannouleas¹, U. Landman¹, A. Herlert², and L. Schweikhard²

¹ School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA
² Institut für Physik, Johannes Gutenberg-Universität, D-55099 Mainz, Germany

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Abstract. Using Penning-trap experiments and a shell-correction method incorporating ellipsoidal shape deformations, we investigate the formation and stability patterns of trianionic gold clusters. Theory and experiment are in remarkable agreement concerning appearance sizes and electronic shell effects. In contrast to multiply cationic clusters, decay of the trianionic gold clusters occurs primarily via electron autodetachment and tunneling through a Coulomb barrier, rather than via fission.

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1 Introduction

While electrical charging of macroscopic metal capacitors has been a familiar subject since the earliest days of electricity [1], only recently the charging of nanostructures emerged as an active research field in diverse areas of condensed-matter, molecular, and cluster physics. The systems involved include semiconductor quantum dots [2], as well as various gas-phase微sysystems such as carbon clusters and fullerenes [3, 4], large organic molecules [5] and metal clusters [6–10].

Although observations [3] of the gas-phase carbon clusters and fullerenes were reported in 1990-1991, the observation of gas-phase multiply anionic metal clusters continued to remain until recently an outstanding experimental challenge. Indeed theoretical studies had been performed several years ago [11(a)], but only recently the first di- anionic metal clusters Au²⁻ were observed [12]. Soon thereafter additional observations of di- and trianionic gas-phase metal clusters for several other materials were reported [13–16].

The case of di- and silver clusters has been discussed in detail elsewhere, both experimentally [13, 16] and theoretically [11(b)]. In the following, we will focus on studying the generation and stability of triply anionic gas-phase metal clusters, in particular of Au³⁻. The theoretical conclusions concerning the stability and decay channels of Au³⁻, as well as their appearance sizes, n³⁻, are fully supported by experimental observations of the production yields [17].

Macroscopic metal capacitors may be charged at will, but for gas-phase metal clusters there are intrinsic limits dependent on the material and the size of the cluster. These limits are due to instabilities arising from the confinement of excess charges to a small volume of microscopic dimensions. Of particular interest is the fact that triply anionic gold clusters behave remarkably differently than their cationic counterparts [18]: they dissociate via a different decay channel, i.e., electron autodetachment through a repulsive Coulomb barrier (CB) [19], instead of fragmenting via fission. Although they differ in their decay channels, the triply charged metal-cluster anions exhibit shape-dependent electronic shell effects [8, 9], in analogy with the neutral and cationic species.

2 Theory

Theoretically, two classes of decay channels need to be considered for the appearance sizes of the Au³⁻ clusters: (i) binary and ternary fission channels,

\[ \text{Au}^3_- \rightarrow \text{Au}^2_\text{p}^- + \text{Au}_\text{n}_- \text{p}, \]  

\[ \text{Au}^3_- \rightarrow \text{Au}^\text{p} + \text{Au}^-_\text{Q} + \text{Au}_\text{n}_- \text{p}_- \text{Q}, \]

which have well known analogs in the case of multiply cationic clusters [6–8] and atomic nuclei [20], and (ii) electron autodetachment via tunneling through a repulsive Coulombic barrier [11],

\[ \text{Au}^3_- \rightarrow \text{Au}^2_\text{p} + e, \]

in analogy to proton and alpha decay in atomic nuclei [20, 21].

For the theoretical analysis of the energetics of these channels, we use a finite-temperature semi-empirical shell-correction method (FT-SCM), which has been previously used successfully to describe the properties of neutral and...
cationic metal clusters [8,9]. This FT-SCM, developed by two of the authors, incorporates three important aspects, namely, triaxial deformations, entropy of the electrons, and thermal effects originating from shape fluctuations.

Since the number of delocalized valence electrons is fixed for a given cluster, \( M_N \), we need to use [22,23] the canonical ensemble in calculating their thermodynamical properties. For determining the free energy, \( F(\beta, N, x) \) (\( \beta = 1/T \)), which incorporates the electronic entropy, we separate it, in analogy with the zero-temperature limit [9(a)], into a smooth, liquid-drop-model part, \( F_{LDM} \), and a Strutinsky-type [24] shell-correction term, \( \Delta F_{sh} \). The shell correction term is specified as the difference \( \Delta F_{sh} = F_{sp} - \tilde{F}_{sp} \), where \( F_{sp} \) is the canonical free energy of the valence electrons viewed as independent single particles in their effective mean-field potential. For calculating the canonical \( F_{sp} \), we adopt a number-projection method [25], according to which

\[
F_{sp} = -\frac{1}{\beta} \ln \left\{ \int e^{-\beta(\mathbf{E}_{sp}(\mathbf{\mu}) + i\phi) e^{-\beta(\mathbf{\mu} + \phi) N_e}} \right\},
\]

where \( N_e \) is the number of electrons and \( \mathbf{\mu} \) is the chemical potential of the equivalent grand-canonical ensemble. The grand-canonical partition function, \( Z_{GC} \), is given by

\[
Z_{GC}(\beta, \mathbf{\mu}) = \prod_i (1 + e^{-\beta(\varepsilon_i - \mathbf{\mu})}),
\]

where \( \varepsilon_i \) are the single-particle levels of the modified Nilsson Hamiltonian pertaining to triaxial shapes [9(a)]. The temperature dependent average \( \tilde{F}_{sp} \) [26] is specified using the same expressions as for \( F_{sp} \), but with a set of smooth levels defined as \( \tilde{\varepsilon}_i = \tilde{E}_{sp}^{osc}(i) - \tilde{E}_{sp}^{osc}(i - 1) \), where \( \tilde{E}_{sp}^{osc}(N_e) \) is the zero-temperature Strutinsky average of the single-particle spectrum of an anisotropic, triaxial oscillator (see section II.C. of Ref. [9(a)]).

The LDM term \( \tilde{F}_{LDM} \) consists of three contributions: a volume, a surface, and a curvature term. Since volume conservation during deformation is assumed, we need not consider the temperature dependence of the corresponding term when calculating observables, such as EA’s or IP’s, associated with processes which do not change the total number of atoms, \( N \). The experimental temperature dependence of the surface tension, \( \sigma(T) = c_0 - c_1 (T - T_{m}) \), is taken from standard tables [27] (\( T_{m} \) is melting-point temperatures [28]), but normalized to yield the \( \sigma(T) = 0 \) value used in our earlier calculations [9(a)]. Since no experimental information is available regarding the curvature coefficient, \( \tilde{A}_x \), we assume the same relative temperature dependence as for \( \sigma(T) \) normalized to the \( T = 0 \) value used earlier [9(a)]. Finally, the expansion of the Wigner- Seitz radius due to the temperature is determined according to the coefficient of linear thermal expansion [28]. With these modifications, the remaining steps in the calculation of \( \tilde{F}_{LDM} \) follow closely section II.A. of Ref. [9(a)].

According to the general theory of thermal fluctuating phenomena [29], the triaxial shapes of the clusters, specified by the \( \beta_H \) and \( \gamma_H \) Hill-Wheeler parameters [30], will explore [31] the free-energy surface, \( F(\beta, N, x; \beta_H, \gamma_H) \), with a probability,

\[
P(\beta_H, \gamma_H) = Z^{-1} \exp\left[ -\beta F(\beta, N, x; \beta_H, \gamma_H) \right],
\]

the quantity \( Z \) being the classical Boltzmann-type partition function,

\[
Z = \int d\tau \exp\left[ -\beta F(\beta, N, x; \beta_H, \gamma_H) \right],
\]

and \( d\tau = \beta_H |\sin(3\gamma_H)| d\beta_H d\gamma_H \) the proper volume element [32]. Thus, finally, the free energy, \( \langle F(\beta, N, x) \rangle \), averaged over the shape fluctuations can be written as

\[
\langle F(\beta, N, x) \rangle = \int \frac{d\tau}{\beta} \langle F(\beta, N, x; \beta_H, \gamma_H) \rangle P(\beta_H, \gamma_H).
\]

The finite-temperature multiple electron affinities of a cluster of \( N \) atoms of valence \( v \) (we take \( v = 1 \) for Au) are defined as

\[
A_x(N, \beta) = F(\beta, vN, vN + x - 1) - F(\beta, vN, vN + x),
\]

where \( F \) is the free energy, \( \beta = 1/k_BT \), and \( x \leq 1 \) is the number of excess electrons in the cluster (e.g., the first, second, and third electron affinities correspond to \( x = 1, x = 2, \) and \( x = 3 \) respectively). The smooth contribution \( \tilde{A}_x(N, \beta) \) to the full multiple electron affinities \( A_x(N, \beta) \) can be approximated by the LDM expression [11(a)],

\[
\tilde{A}_x = \tilde{A}_1 - \frac{(x - 1)\gamma^2}{\gamma + \delta_0} = W - \frac{(x - 1)^2 \gamma^2}{R(N) + \delta_0},
\]

where \( R(N) = r_s N^{1/3} \) is the radius of the positive background \( (r_s \) is the Wigner-Seitz radius which depends weakly on \( T \) due to volume dilation), \( \gamma = 5/8, \delta_0 \) is an electron spillout parameter. For simplicity, the work function \( W \) is assumed to be temperature independent [we take \( W(Au) = 5.31 \text{ eV} \)].

3 Experiment

Trianionic gold clusters have been produced and observed by use of a Penning trap system devoted to metal cluster research [33]. The present procedure is the same as for the case of dianionic silver clusters as described in detail elsewhere [16]: Singly charged clusters Au\(_N^++\) from a Smalley-type ion source [34] are transferred by ion-optical elements through differential-pumping stages and captured in flight in a Penning trap [35]. This device acts as a wall-less container for ions by the combination of a strong magnetic field and an electric trapping potential along the magnetic field lines [36].

After size selection the clusters of interest are subjected to the presence of simultaneously stored electrons which are created by electron-impact ionization of argon atoms inside the trap volume. The clusters are observed to
pick up one or two further electrons. This reaction is analyzed by time-of-flight mass spectrometry after axial ejection of the cluster ions. A typical experimental sequence lasts a few seconds and a few tens of ions are observed in each experimental cycle by single-ion counting. The signal intensity of several hundred sequences is summed to increase the statistical significance of the data.

The electron pickup is influenced by many experimental conditions. However, if the parameters are kept constant the relative conversion yields are found to give valuable information on the clusters’ properties. In particular, it has been suggested [11(b), 12, 13] that the resulting experimental yield patterns reflect the clusters’ multiple electron affinities. The case of Au$_N$$^{-3}$ considered here and that of Ag$_N$$^{-3}$ [16] show this to be a general feature applicable to any excess charge and cluster species.

4 Results

In Fig. 1(a), we display the SCM theoretical results [37,38] for the second, A$_2$, and third, A$_3$, electron affinities of Au$_N$ clusters in the size range 50 \( \leq N \leq 70 \). Multiply anionic clusters M$_N^-$ with A$_2$ \( < 0 \) are unstable [11] against electron emission via tunneling through a CB. In the case of doubly anionic gold clusters, all sizes in the aforementioned range are stable, i.e., they have A$_2$ \( > 0 \) [see upper curve in Fig. 1(a)]. In contrast, for the gold-cluster trianions, those with N \( \leq 53 \) and 56 \( \leq N \leq 62 \) have A$_3$ \( < 0 \). Thus, the appearance size for Au$_N$$^{-3}$ is \( \approx 54 \). Apparently, the major shell closure at 58 electrons (corresponding to the Au$_{56}^3$ parent of the triply charged Au$_{56}^3$ cluster) creates an island of stability (the clusters with \( N = 54 \) and 55 have A$_3$ \( > 0 \) preceding the main stability branch (with \( N \geq 63 \)).

Figure 1(b) shows the observed relative abundances for Au$_N$$^{-2}$ and Au$_N$$^{-3}$ in the same size range. Day-to-day variations of the experimental parameters lead to values that differ somewhat more than expected from the statistical uncertainties of the individual measurements. (In general the variations of the trianion values correspond to those of the dianions.)

While dianionic gold clusters are observed for all sizes under investigation (50 \( \leq N \leq 70 \)) as expected [11(b), 13] \( \{ \nu_3^2(\text{Au}) = 12 \} \), there is no obvious structure in the dianionic clusters in the size range 50 \( \leq N \leq 70 \). Theoretical results from SCM calculations are connected by a solid line, and LDM results [see Eq. (10) with \( x = 2 \) and 3] are depicted by the dashed lines. (b) Experimental relative abundances of Au$_N$$^{-2}$ (open circles) and Au$_N$$^{-3}$ (full circles) as observed after simultaneous storage of Au$_N$ and electrons in the Penning trap. (The statistical uncertainties of the individual Au$_N$$^{-2}$ and Au$_N$$^{-3}$ values are smaller than the symbol size.)

With respect to the general trend and with the presence of the promonitory around \( N = 55 \) in front of the principal branch of the Au$_N$$^{-3}$ clusters. Comparison of the shell-corrected results (solid dots) with the LDM curve (dashed line) further highlights that electronic shell effects underlie the calculated detailed patterns for A$_3$ shown in Fig. 1(a) and those observed experimentally in Fig. 1(b).

To explore the energetic stability of the Au$_N$$^{-2}$ clusters against binary (b) and ternary (t) fission [see Eqs. (1) and (2)], we show in Fig. 2 SCM results for the fission dissociation energies, \( \Delta_{N;\gamma} \) \( (\gamma = b \text{ or } t) \), associated with the most favorable channel for a given parent Au$_N$$^{-2}$ cluster. We found that the most favorable channel corresponds to the generation of one or two closed-shell Au$^{-i}$ anions in the case of binary and ternary fission, respectively. Thus \( \Delta_{N;b} = F(\text{Au}^{-i}) + F(\text{Au}^{2-i}_{N-1}) - F(\text{Au}^{-i}_N) \) and \( \Delta_{N;t} = 2F(\text{Au}^{-i}) + F(\text{Au}^{2-i}_{N-2}) - F(\text{Au}^{-i}_N) \), with the total free energies of the multiply anionic parent and the charged fission products calculated at \( T = 300 \) K. The fission results
summarized in Fig. 2 for the most favorable channel illustrate that exothermic fission (that is $\Delta_{N,\gamma}^{1-} < 0$) occurs only for the smallest sizes ($N \leq 25$). This, together with the existence of a fission barrier, leads us to conclude that the stability of Au$_N^{3-}$ clusters is dominated by the electron autodetachment as the prevalent channel governing the clusters’ stability. Finding (iii) holds for doubly charged clusters, too [11(b), 13], and leads to appearance sizes unrelated to those known from the more familiar case of multiply charged cationic clusters. It will be of interest to further explore the properties of stored multiply-charged metal cluster anions by either collisional or photo activation [40], as well as to investigate their chemical properties [41].

5 Summary

We studied the generation and stability patterns of the Au$_N^{3-}$ clusters via Penning-trap experiments and theoretical SCM investigations and found the following: (i) there is a remarkable agreement between the theoretically predicted and the measured appearance size [$n_{3-}^{N}$ (Au) = 54]; (ii) the measured yields near the threshold are strongly modulated revealing the influence of electronic shell effects; and (iii) rather than fragmentation via fission, we identified electron autodetachment as the prevalent channel governing the clusters’ stability. Finding (iii) holds for doubly charged clusters, too [11(b), 13], and leads to appearance sizes unrelated to those known from the more familiar case of multiply charged cationic clusters. It will be of interest to further explore the properties of stored multiply-charged metal cluster anions by either collisional or photo activation [40], as well as to investigate their chemical properties [41].

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38. For Au$_N^{-2}$ clusters, the $T = 0$ parameters entering in the SCM calculation (for definitions see Ref. [9(a)]) are $U_0 = -0.045$, $r_s = 3.01$ a.u., $t = 0.37$ a.u., $\delta_0 = 1.31$ a.u., $\delta_2 = 0$, $W = 5.31$ eV, $\alpha_c = -8.06$ eV, $\alpha_s = 2.52$ eV, and $\alpha_c = 1.04$ eV. For an additional explanation, see footnote 17 in Ref. [9(b)]. The temperature dependence of the surface tension and the coefficient of linear thermal expansion were taken from standard tables.
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