Two-dimensional magic numbers in mass abundances of photofragmented bimetallic clusters

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Abstract. The stability of cationic gold clusters doped with one transition metal atom was investigated by a mass spectrometric analysis of fragments resulting from high fluence irradiation of a cluster beam. Strongly enhanced abundances are found for Au$_5$X$^+$, X = V, Mn, Cr, Fe, Co, Zn, which implies that these species are far more stable towards fragmentation than their neighbouring cluster sizes. Here we interpret the enhanced stability of these clusters within a shell model approach for two-dimensional (2D) systems: the number of delocalized electrons in Au$_5$X$^+$ is six, which is a magic number for 2D systems. Quantum chemical calculations for Au$_N$Zn$^+ (N = 2–6)$ predict planar structures that are stabilized by the influence of the dopant atom. Also, the main features of the calculated molecular orbitals are well reproduced by a simple electron-in-a-box model. The present report constitutes the first observation of 2D magic numbers in size dependent properties of metal clusters.

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1. Introduction

Basic properties of physical systems composed of a limited number of fermions, such as atoms and atomic nuclei, are successfully described by simple shell models [1, 2], which have been gratefully adopted to explain size-dependent properties of metal nanoclusters [3, 4], and semiconductor quantum dots [5, 6]. Particularly important for all these few-fermion systems is their shape and symmetry. While spherical models usually describe their properties fairly well in the vicinity of closed shells, lower symmetries (ellipsoidal or spheroidal Jahn–Teller distorted structures) are needed to describe size-dependent properties over larger size ranges [7, 8].

Gas phase clusters composed of alkali elements (and to a lesser extent also coinage, di-, and trivalent metals) show pronounced size-dependent features in most of their properties, originating from the delocalization of atomic valence electrons over the cluster, which results in an electronic shell structure and corresponding magic numbers as predicted by Ekardt [3]. First mass spectrometric observations of magic numbers corresponding to completely filled spherical electron shells were reported by Knight et al [4]. These and more elaborate measurements of properties such as ionization potentials, electron affinities or photoabsorption cross sections [9] were well explained by theories with various degrees of sophistication, including phenomenological shell models, jellium models and \textit{ab initio} quantum chemical calculations [10].

In nuclear physics, detailed understanding of nuclear structure emerged only by accessing short-lived nuclei far from stability as produced in nuclear reactions. That way, e.g. shape changes and shape coexistence (nuclear isomers) were identified as resulting from a delicate energy balance related to the number of composing fermions (neutrons and protons) [11]. A similar route for investigating substantially different metal clusters is available through the production of bimetallic clusters. Here the number of fermions (the number of delocalized electrons governs the shell model interpretations) and the confining potential (formed by the ion cores) can be changed independently. Since the cluster structure largely influences the shape of the mean field potential experienced by the delocalized electrons, shell structure modifications related to the cluster geometry are to be expected [12].

We systematically investigated the stability as a function of size and composition of gold clusters doped with trivalent metal atoms or with 3d transition metal atoms. For Au clusters with a single dopant atom, mass abundance oscillations such as steps and peaks could be related to magic numbers stemming from spherical shell models, where closed shells correspond to filled energy levels for itinerant electrons in the cluster [13, 14]. In this paper we present and discuss evidence for the existence of a two-dimensional (2D) shell structure for specific doped gold clusters. Mass spectrometric analysis of bimetallic Au\textsubscript{N}X\textsuperscript{+} clusters (X = V, Cr, Mn, Fe, Co, Zn) showed that species with N = 5 have an anomalously high abundance, indicating a particularly high stability. According to the spherical shell model interpretation that successfully explained the stability patterns observed in mass spectra of the larger Au\textsubscript{N}X\textsuperscript{+} clusters [14], the Au\textsubscript{5}X\textsuperscript{+} species contain six delocalized electrons. Indeed, \textit{ab initio} quantum chemical calculations for Au\textsubscript{5}Zn\textsuperscript{+} indicated delocalization of six electrons in orbitals very similar to aromatic organic molecules such as C\textsubscript{6}H\textsubscript{6} and C\textsubscript{5}H\textsubscript{5}\textsuperscript{−} (except for their nodal properties in the molecular plane) [15]. Here we present calculations for Au\textsubscript{N}Zn\textsuperscript{+} clusters, with N ranging from two to six, predicting planar ground-state shapes for all these species, and argue that the anomalous stability of the Au\textsubscript{5}X\textsuperscript{+} clusters is related to the delocalization of six electrons, which is a magic number for 2D structures. This is corroborated by a one-to-one match between the molecular orbitals calculated by the \textit{ab initio} method and the wavefunctions of an electron in a planar box.
2. Photofragmentation experiments

Beams of Au\(_N\)X\(_M\) (X = Cr, Co, Zn, N = 1–25, M = 0–4) clusters were produced with a dual-target dual-laser vaporization source [16], where atom condensation of two different metal elements into mixed clusters is initiated by introducing helium gas into the source. The relative stability of cationic clusters was investigated by photofragmentation, following irradiation of the cluster beam with high intensity ArF laser light (>2 MW cm\(^{-2}\), 10 ns pulses, 6.43 eV photon energy), and time-of-flight mass spectrometry analysis of the resulting cationic fragments. The photofragments show a size distribution with an enhanced abundance, or steps in abundance, for specific cluster sizes or cluster compositions: clusters with an enhanced stability will be more abundant.

Mass abundance spectra recorded after photofragmentation of gold clusters mixed with chromium, cobalt or zinc atoms are shown in figure 1. The highest peaks in the spectra correspond to pure Au\(_N^+\) clusters. To the right-hand side of the pure gold clusters, peaks corresponding to the Au\(_N\)X\(_+\) clusters appear; they are connected with a red line. Other peaks in the spectra relate to Au\(_N\)X\(_M^+\) with \(M = 2–4\). In this paper we will concentrate on gold clusters containing one dopant atom only. For those, the experimental spectra reveal an odd–even staggering (clusters with an even number of delocalized electrons are more stable) and drops in abundance after specific cluster sizes. Most of these observations can be interpreted and explained within a spherical shell model picture (and corresponding magic numbers) and provide information on the electronic behaviour of the dopant atoms in the cluster. Such an analysis for gold clusters doped with all 3d transition metals is presented elsewhere [14]. Here we will focus on the most pronounced feature in the mass spectra, namely the much higher abundance for doped clusters with five gold atoms in comparison to the neighbouring sizes.

More quantitative information on the stability of the clusters can be obtained by relating the experimentally observed peak heights \(I_N\) to the second difference in Helmholtz free energy \(\Delta^2 F_N = 2F_N - F_{N+1} - F_{N-1}\) [17]:

\[
\ln \left( \frac{I_N}{I_{N+1}} \right) = \frac{\Delta^2 F_N}{k_B T}.
\]

For Au\(_N\)Zn\(^+\) (\(N = 2–10\)) this quantity is given in figure 2(b) as a function of size, in comparison with the abundances shown in figure 2(a) (red curve in figure 1(c)). The plotted value for a given \(N\) can be interpreted as the difference between fragmentation energies of Au\(_{N+1}\)Zn\(^+\) into Au\(_N\)Zn\(^+\) and a Au atom, and Au\(_N\)Zn\(^+\) into Au\(_{N-1}\)Zn\(^+\) and a Au atom, where positive values indicate that the dissociation of Au\(_{N+1}\)Zn\(^+\) is more favourable, i.e., that Au\(_N\)Zn\(^+\) is more stable. This way the experiments clearly indicate an enhanced stability for Au\(_5\)Zn\(^+\). For zinc doped gold clusters quantum chemical calculations of structural and electronic properties were performed, allowing a detailed comparison between experiments and theory.

3. Quantum chemical calculations for Au\(_N\) Zn\(^+\) (\(2 \leq N \leq 6\))

Geometry operators of Au\(_N\)Zn\(^+\) (\(2 \leq N \leq 6\)) were performed at the MP2 level of theory with Gaussian 98 [18]. A relativistic effective core potential with corresponding valence electron basis set (Lanl2dz) was adopted for Au [19]; the Wachters–Hay all-electron basis sets (6 – 311 + G(d) basis sets in Gaussian 98) were used for Zn [20]. Lowest energy structures for the calculated clusters are shown in figure 3; all these structures are planar. Although several isomers exist.
Figure 1. Mass abundance spectra showing the cluster ion signals following photofragmentation with high fluence ArF excimer laser light (wavelength 193 nm) for $\text{Au}_N \text{Cr}_M^+$ (a), $\text{Au}_N \text{Co}_M^+$ (b) and $\text{Au}_N \text{Zn}_M^+$ (c) ($N = 1–25$, $M = 0–4$) as a function of the number of gold atoms in the cluster. The peaks corresponding to $\text{Au}_N X^+$ are connected with a red line. Notice the strongly enhanced abundance for $N = 5$.

for $N > 2$, hardly any 3D structures were found at low excitation energy\(^1\). Dissociation energies ($\Delta H_{0N}$) calculated as first differences in zero-temperature enthalpies for the reaction $\text{Au}_N \text{Zn}^+ \rightarrow \text{Au}_{N-1} \text{Zn}^+ + \text{Au}$ are shown in figure 2(c); second differences ($\Delta_2 H_{0N}$) are plotted in figure 2(d)\(^2\). This quantity, plotted as a function of size, qualitatively reproduces the main features of the ratio of cluster ion signals\(^3\) ($\ln(I_N/I_{N+1})$).

\(^1\) For $N = 6$ a 3D structure, less stable by 1.7 eV than the lowest energy structure, was found in which two Au\(_3\) triangles are perpendicularly connected through the Zn atom.

\(^2\) Other dissociation channels of $\text{Au}_N \text{Zn}^+$, for instance the channels losing Au\(_2\), Zn\(^+\) or Au\(^+\), were calculated to give dissociation energies larger than the channel losing a Au atom. Therefore, we assume that the observed stability pattern is governed by a monomer evaporation process in which $\text{Au}_N \text{Zn}^+$ loses Au atoms one by one.

\(^3\) According to equation (1) the logarithmic cluster abundance ratio should be compared to the second difference in Helmholtz free energy ($\Delta_2 F_N$), which equals $\Delta_2 H_{0N}$ for zero temperature. Furthermore, quantitative agreement only can be expected if the dissociation process is accounted for, which would require us to calculate the full potential energy surface.
Figure 2. The peak heights of the experimental $\text{Au}_N\text{Zn}^+$ ($N = 1–10$) spectrum are given in (a). The logarithm of the ratio of cluster ion signals (equation (1)) is plotted for $\text{Au}_N\text{Zn}^+$ in (b). Calculated dissociation energies for the reaction $\text{Au}_N\text{Zn}^+ \rightarrow \text{Au}_{N-1}\text{Zn}^+ + \text{Au}$ and second differences in zero-temperature enthalpies are given respectively in (c) and (d). Notice the qualitative agreement between the experimental logarithmic ratios of cluster ion signals (b) and the calculated second differences in zero-temperature enthalpies (d) (see footnote 3). HOMO–LUMO energy gaps for $\text{Au}_N\text{Zn}^+$ are given in (e), showing an enhancement for $N = 5$ compared to the neighbouring sizes.

The dopant Zn atom significantly affects the electronic structure of the $\text{Au}_N\text{Zn}^+$ clusters. Apart from the expected ‘normal’ $\sigma$ bonding between valence Zn 4s and Au 6s orbitals, the Zn atom forms extra $\sigma$ bonding with the Au atoms through an overlap between vacant in-plane Zn 4p orbitals and valence Au 6s (and 5d) orbitals. This bonding interaction enhances the planarity (for the smaller clusters the linearity) of the clusters, because the s–p overlap is maximized when both Au and Zn atoms are in the same plane (or on the same line). A physically similar effect was found to be responsible for the planarity of pure anionic Au clusters [21]. In that case the relativistic effects of the Au atoms effectively reduce the 6s orbitals in size, enhancing the in-plane overlap between the 5d orbitals. Another result of this interaction is the stabilization of the HOMO of $\text{Au}_N\text{Zn}^+$. The s–p overlap, which is responsible for the bonding character...
between Au and Zn in the HOMO, has a stabilizing effect on the HOMO. The energy lowering of the HOMO results in a large HOMO–LUMO energy gap of the Au$_N$Zn$^+$ clusters (figure 2(e)).

4. Two-dimensional magic numbers

It is tempting to describe the enhanced stability for the clusters with five gold atoms as due to a closed electron shell in a simple delocalized electron shell model, as was done successfully before for pure noble metal clusters [9, 22]. In the case of zinc-doped clusters, assuming that for each gold atom one valence electron ($6s^1$), and for the zinc atom two valence electrons ($4s^2$), are delocalized over the cluster volume, the number of delocalized electrons for the cationic Au$_5$Zn$^+$ adds up to six. Also, for the open 3d-shell transition elements V, Mn, Cr, Fe and Co, two valence electrons will be itinerant [14]. In the following, we will argue that the observed enhanced stability for a cluster with six delocalized electrons is consistent with six being a 2D magic number, analogous to semiconductor quantum dots and aromatic 2D ring structures.

Hereto, we have considered the solution of the Schrödinger equation for the simple ‘electron-in-a-box’ problem. For an infinitely high square potential well shaped as an equilateral 2D triangle with side $a$, the energy levels are given by ($\hbar$ is Planck’s constant, and $m$ is the electron mass)

$$E(p, q) = E_0(p^2 + pq + q^2) \quad \text{with} \quad E_0 = \frac{2\hbar^2}{3ma^2}.$$  \hspace{1cm} (2)

The quantum numbers $q$ and $p$ depend on the irreducible representations of the $C_{3v}$ symmetry group and are ($q = 0, 1, 2, \ldots$) and ($p = q+1, q+2, q+3, \ldots$) for $A_1$ symmetry, ($q = 1, 2, 3, \ldots$) and ($p = q+1, q+2, q+3, \ldots$) for $A_2$ symmetry and ($q = 1/3, 2/3, 4/3, 5/3, \ldots$) and ($p = q+1, q+2, q+3, \ldots$) for the twofold degenerate $E$ symmetry [23]. The energy
Ab initio calculations
Au\textsubscript{5}Zn\textsuperscript{+}, C\textsubscript{2v}-symmetry

Electron in a triangular box

(a) E = -3.5 eV
(q=0, p=1)

(b) E = -3.6 eV
(q=1/3, p=4/3)

LUMO

(a') E = -3.8 eV
LUMO

HOMO

(a) E = -12.1 eV
(q=0, p=2)

(b) E = -12.4 eV
(q=2/3, p=5/3)

(b') E = -15.9 eV
(q=0, p=1)

Figure 4. (a) The molecular orbital patterns of HOMO and LUMO levels for the Au\textsubscript{5}Zn\textsuperscript{+} cluster with C\textsubscript{2v} symmetry, calculated at the MP2 level of theory. Animated versions are available (Cortona molecular orbital visualization software can be downloaded, free of charge, at http://www.parallelgraphics.com/products/cortona/). (b) One-electron wavefunctions for an electron confined in an infinitely high potential well with a 2D equilateral triangular shape (see footnote 4). The second and fourth levels in (b) are degenerate due to the higher symmetry. Note the striking similarity of the orbital patterns in (a) and (b), indicating a strongly delocalized character of the valence electrons in this small Zn-doped gold cluster cation.

levels with corresponding quantum numbers and wavefunctions are plotted in figure 4(b)\textsuperscript{4}. As could be anticipated for a 2D system, a large energy gap appears when the second degenerate level is filled (total of six electrons). Similar calculations for different symmetries (circle or square) show essentially the same behaviour: six is an obvious magic number associated with a

\textsuperscript{4} The following parameters were chosen in order to obtain energies and sizes consistent with the results of the \textit{ab initio} calculations: $a = 7$ Å ($5$ Å side of the ion structure + $2 \times$ an electron spill-out of $1$ Å), bottom of the infinitely high potential well at $-20$ eV.

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Figure 5. Energy levels for 2D (infinitely high) square well potentials with triangular (a), circular (b) and square (c) symmetry. The energy is given in $E^* = \frac{\hbar^2}{8mA}$, where $m$ is the electron mass and $A$ is the surface area of the 2D structure. In all cases, six delocalized electrons correspond to a magic number.

large shell gap\(^5\). The energy levels in an infinitely high potential well with square, circular and triangular geometry are schematically drawn in figure 5.

Striking is the strong resemblance of the electron wavefunction patterns calculated for this very simple 2D system (shown in figure 4(b)) with the molecular orbitals of the C\(_{2v}\) Au\(_5\)Zn\(^+\) cluster obtained with the relativistic quantum chemical calculation (shown in figure 4(a)). Obvious similarities in the main features of the orbital patterns are observed, which indicates that the six valence electrons that occupy the three HOMO levels in Au\(_5\)Zn\(^+\) largely behave as delocalized within the 2D triangularly shaped planar cluster.

An inspection of data reported in recent literature yielded corroborating evidence for six delocalized electrons being a 2D magic number in metal clusters, in particular for gold cluster anions where Au\(_5^-\) appears to be magic. In a mass spectrometric study of Au\(_{N^-}\) a steplike feature is observed at $N = 5$, after Au\(_5^-\) [25]. Another piece of information is provided by the measurement of the electron affinities (EAs) of gold anionic clusters as a function of size. While for other coinage metal clusters (copper and silver) a drop of the EA occurs at $N = 8$,

\(^5\) A recent investigation of shell structures for deformed 2D electron gas clusters in an ultimate jellium assumption reached the same conclusions [24]. In a self-consistent Kohn–Sham approach, ground-state energies per electron calculated as a function of size showed a distinctive step for six electrons. For this size ground-state density contours were very similar to the contours that can be deduced from the orbitals shown in figure 4 for Au\(_5\)Zn\(^+\).

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for gold there is a clearly lower value for $N = 6$ [26]. This was interpreted as evidence for the non-validity of spherical shell model descriptions for gold clusters, while in view of the argumentation developed here it may be a strong indication that small gold anionic clusters have a planar shape. Indeed, recent density functional theory calculations including scalar-relativistic 

*ab initio* pseudopotentials predicted planar structures for small gold cluster anions [27], and ion mobility investigation showed $\text{Au}_N^-$ to be planar up to $N = 12$ [28].

5. Conclusion

Photofragmentation experiments on bimetallic $\text{Au}_N X^+$ ($X = \text{V, Mn, Cr, Fe, Co and Zn}$) have shown a strongly enhanced abundance for $\text{Au}_5 X^+$. *Ab initio* calculations predicted that $\text{Au}_N \text{Zn}^+ (N = 2–6)$ are planar and that $\text{Au}_5 \text{Zn}^+$ has six delocalized electrons. We argued that the high stability of these particular doped gold clusters with six delocalized electrons is related to their planar shape and corresponds to a magic number for electrons in a 2D box also present in other 2D quantum systems such as semiconductor quantum dots. It is the first time that the presence of six delocalized electrons in a metallic cluster has been revealed as a possible cause of a pronounced enhanced stability. This way the mass spectra of $\text{Au}_N X^+$ cations prove that small 2D magic clusters exist next to the well known magic clusters with a spherical shape.

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References

[1] Bohr N 1913 On the constitution of atoms and molecules Phil. Mag. 26 1–25
[2] Mayer M G 1948 On closed shells in nuclei Phys. Rev. 74 235–9
[3] Ekardt W 1984 Dynamical polarizability of small metal particles, self-consistent spherical jellium background model Phys. Rev. Lett. 52 1925–8
[4] Knight W D, Clemenger K, de Heer W A, Saunders W A, Chou M Y and Cohen M L 1984 Electronic shell structure and abundances of sodium clusters Phys. Rev. Lett. 52 2141–3
[5] Tarucha S, Austing D G, Honda T, vanderHage R J and Kouwenhoven L P 1996 Shell filling and spin effects in a few electron quantum dot Phys. Rev. Lett. 77 3613–16
[6] Kouwenhoven L P, Austing D G and Tarucha S 2001 Few-electron quantum dots Rep. Prog. Phys. 64 701–36
[7] Nilsson S G 1955 Binding states of individual nucleons in strongly deformed nuclei Mat.-Fys. Medd. K. Dan. Vidensk. Selsk. 29
[8] Clemenger K 1985 Ellipsoidal shell structure in free-electron metal clusters Phys. Rev. B 32 1359–62
[9] For a review, see:

    de Heer W A 1993 The physics of simple metal clusters: experimental aspects and simple models Rev. Mod. Phys. 65 611–76

*New Journal of Physics* 5 (2003) 46.1–46.10 (http://www.njp.org/)
[10] For a review, see: Brack M 1993 The physics of simple metal clusters: self-consistent jellium model and semiclassical approaches Rev. Mod. Phys. 65 677–732

[11] A recent example of identification of shape coexisting neutron deficient nuclei was reported in: Andreyev A et al 2000 A triplet of differently shaped spin-zero states in the atomic nucleus $^{186}$Pb Nature 405 430–3

[12] Yeretzian C 1995 Electronic structure effects in bimetallic M$_x$N clusters (M = alkali, N = divalent metal) J. Phys. Chem. 99 123–30 and references therein

[13] Bouwen W, Vanhoutte F, Despa F, Bouckaert S, Neukermans S, Kuhn L T, Weidele H, Lievens P and Silverans R E 1999 Stability effects of Au$_N$X$_M^+$ (X = Cu, Al, Y, In) clusters Chem. Phys. Lett. 314 227–33

[14] Neukermans S, Janssens E, Tanaka H, Silverans R E and Lievens P 2003 Element and size dependent electron delocalization in Au$_N$X$^+$ clusters (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni) Phys. Rev. Lett. 90 33401

[15] Tanaka H, Neukermans S, Janssens E, Silverans R E and Lievens P 2003 $\sigma$ aromaticity of the bimetallic Au$_N$Zn$^+$ cluster J. Am. Chem. Soc. 125 2862–3

[16] Bouwen W, Thoen P, Vanhoutte F, Bouckaert S, Despa F, Weidele H, Silverans R E and Lievens P 2000 Production of bimetallic clusters by a dual-target dual-laser vaporization source Rev. Sci. Instrum. 71 54–8

[17] Klots C E 1988 Evaporation from small particles J. Phys. Chem. 92 5864–8

[18] Frisch M J et al 1998 Gaussian 98 revision A.7 (Pittsburgh, PA: Gaussian)

[19] Hay P J and Wadt W R 1985 Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals J. Chem. Phys. 98 299–310

[20] Wachters A J H 1970 Gaussian basis sets for molecular wavefunctions containing third-row atoms J. Chem. Phys. 52 1033–6

Hay P J 1977 Gaussian basis sets for molecular calculations. The representation of 3d orbitals in transition-metal atoms J. Chem. Phys. 66 4377–84

[21] Håkkinen H and Landman U 2000 Gold clusters (Au$_N$, $2 \leq N \leq 10$) and their anions Phys. Rev. B 62 R2287–90

[22] Katakuse I, Ichihara T, Fujita Y, Matsuo T, Sakurai T and Matsuda H 1985 Mass distributions of copper, silver and gold clusters and electronic shell structure Int. J. Mass Spectrom. Ion. Process. 67 229–36

[23] Li W K and Blinder S M 1985 Solution of the Schrödinger equation for a particle in an equilateral triangle J. Math. Phys. 26 2784–6

[24] Reimann S M, Koskinen M, Helgesson J, Lindelof P E and Manninen M 1998 Deformations of quasi-two-dimensional electron gas clusters Phys. Rev. B 58 8111–19

[25] Stoermer C, Friedrich J and Kappes M M 2001 Observation of multiply charged cluster anions upon pulsed UV laser ablation of metal surfaces under high vacuum Int. J. Mass Spectrom. 206 63–78

[26] Taylor K J, Pettiette-Hall C L, Cheshnovsky O and Smalley R E 1992 Ultraviolet photoelectron-spectra of coinage metal clusters J. Chem. Phys. 96 3319–29

[27] Håkkinen H, Moseler M and Landman U 2002 Bonding in Cu, Ag, and Au clusters: relativistic effects, trends, and surprises Phys. Rev. Lett. 89 033401

[28] Furche F, Ahlrichs R, Weis P, Jacob C, Gilb S, Bierweiler T and Kappes M M 2002 The structures of small gold cluster anions as determined by a combination of ion mobility measurements and density functional calculations J. Chem. Phys. 117 6982–90