

Production of dianionic and trianionic noble metal clusters in a Penning trap

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Abstract

Metal clusters, Au_n^- , Ag_n^- , and Cu_n^- , from a laser vaporization source are transferred to a Penning trap and subjected to a bath of simultaneously stored electrons. After some reaction period multiply charged anionic gold, silver, and copper clusters are observed if the clusters under investigation are large enough. The cluster sizes for the onset of the formation of dianions and trianions are compared to a charged sphere model. The description of the experimental findings is largely improved if the repulsive Coulomb barrier is taken into account which prevents autodetachment of the surplus electrons on the experimental time scale of a second.

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1. Introduction

Multiply charged anionic systems are the subject of increased recent interest [1,2]. In the case of dianions, various molecules and clusters have been produced with different experimental techniques, which involve e.g., carbon cluster dianions, C_n^{2-} ($n \geq 7$), from sputter ion sources [3–6], dianionic metal-tetrahalide molecules produced with electrospray ion sources [7–9], and fullerenes C_{60}^{2-} formed after laser desorption from a target [10,11].

The stability of multiply charged anions against electron emission is influenced by the repulsive Coulomb barrier of the corresponding decay products [12,13]. In cases where their electron affinity is negative, tunneling through the Coulomb barrier leads to autodetachment of electrons. Thus, metastable states have been found: The repulsive Coulomb barrier has been directly observed for citric acid dianions by use of photoelectron spectroscopy [14] and delayed electron emission due to tunneling has been reported in case of platinum-tetrahalide dianions [15,16].

As for the production of polyanionic species, the Coulomb repulsion hinders or even prevents the attachment of further electrons. In case of metal clusters, the charging of monoanions has been achieved by the application of an electron bath in a Penning trap [17,18]. Gold cluster dianions [19] and trianions [20] as well as silver cluster dianions have been observed [21]. The relative production yield of multiply charged metal cluster anions as a function of cluster size shows a characteristic pattern due to shell structures of the atomic valence electrons and can be related to the well-known “magic numbers” in the Jellium model [22]. Note, that in addition to the production of multiply charged metal clusters in a Penning trap, gold and platinum cluster dianions and platinum cluster trianions have been observed after laser ablation from a metal target under high vacuum conditions [23,24].

In this work, earlier investigations of the production of doubly and triply charged metal cluster anions in a Penning trap are extended to copper di- and trianions and trianionic silver clusters and the yields of dianionic gold clusters are remeasured. Together with the previous results the new data give a comprehensive overview of the noble metals. The experimental findings are compared to a charged sphere model where the Coulomb barrier is taken into account. The Coulomb barrier is shown to act as a stabilizing factor which can, depending on the clusters’ charge state and

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size, prevent the immediate autodetachment of the surplus electrons.

2. Experimental setup and procedure

The Cluster Trap has been described in detail earlier [25,26] and has been reviewed more recently [27–31]. In short, singly charged noble metal cluster anions are produced in a pulsed laser vaporization/expansion source [32,33] and transferred by ion-optical elements to a Penning trap. They are captured in flight [34], size selected and subjected to an electron bath. After a preset reaction period, the clusters stored in the trap are axially ejected and analyzed by time-of-flight (TOF) mass spectrometry.

The measurements are performed for one cluster size at a time. In order to increase the number of cluster anions, several cluster bunches from the cluster source are accumulated in the trap [35]. For the production of size-selected cluster ensembles, clusters of different sizes than that of interest are radially ejected out of the trap by dipolar excitation of their cyclotron motion [36]. To allow these kinds of manipulations of the ion motion inside the trap, its ring electrode is segmented and rf signals are applied in addition to the static trapping fields. While the resolution of the TOF mass spectrometer is relatively low and only allows to distinguish between the cluster sizes, the ejection has a much higher mass resolving power. Cluster-size selection gives the possibility to observe dissociative electron attachment. However, so far, reactions of this nature have not been observed, nor any dissociation induced by electron impact. The latter could in principle be expected in the next step of the experimental sequence, where a beam of electrons (kinetic energy about 70 eV) is guided through the trap. In the case of cations this leads to further ionization and the observation of extended dissociation reactions [37,38].

The electrons originate from an electron gun located half way between the cluster source and the Penning trap, slightly off-axis. They are guided along the magnetic field lines axially through the center of the trap. The electron beam is applied for one second. During this time argon gas is pulsed into the trap region. In order to avoid ion loss due to collisions of the monoanions with the gas atoms, a quadrupolar excitation of the singly charged cluster anions is applied to axialize the clusters [39,40].

Secondary electrons from the ionization of argon are stored simultaneously with the cluster anions. Note, that for the present investigations the mass ratio between clusters and electrons is up to and above 10^7 . If the trapping potential is sufficiently high [41], multiply charged clusters are observed after some reaction period. For the present experiments a trapping potential of $U_0/2 = 6$ V has been chosen, where U_0 is the static potential between the endcap and ring electrodes of the Penning trap [42].

As an example for the attachment of electrons to stored clusters, Fig. 1 shows TOF mass spectra which are taken in

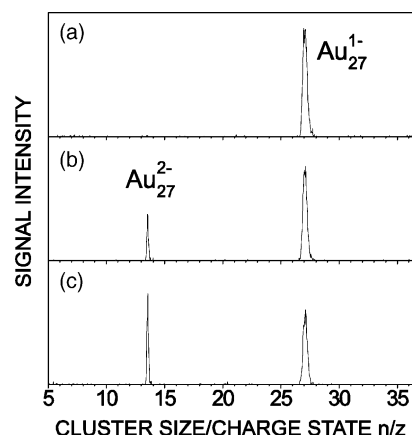


Fig. 1. TOF mass spectra after selection of anionic gold clusters Au_{27}^- (a) and after the application of an electron bath for (b) 1 s and (c) 8 s. The mass spectra have been normalized with respect to the total number of mono- and dianions.

the case of size-selected gold clusters Au_{27}^- immediately after the production of the electron bath (Fig. 1a) and after a shorter and longer period of the clusters in the electron bath (Fig. 1b and c), respectively). For the measurements of Fig. 1, the dianions formed during the application of the electron beam have been ejected in a second ion-selection step, in order not to confuse them with those produced later. Thus, immediately after the creation of the electron bath, no dianions are observed (Fig. 1a). After a reaction period of one second about 15% of the monoanions have been transformed to dianions Au_{27}^{2-} (Fig. 1b) and after 8 s approximately 40% of Au_{27}^- have attached another electron (Fig. 1c). Note, that no dissociative attachment is observed as already mentioned above. Each experimental cycle leads to a few single-ion counts (typically around 40). The sequence is therefore repeated several 10–100 times in order to increase the statistical significance of the data.

When the reaction period is varied, i.e., the time between the creation of the electron bath and the TOF analysis, the transformation of monoanionic to dianionic clusters can be followed as a function of time (Fig. 2). Again, for this series

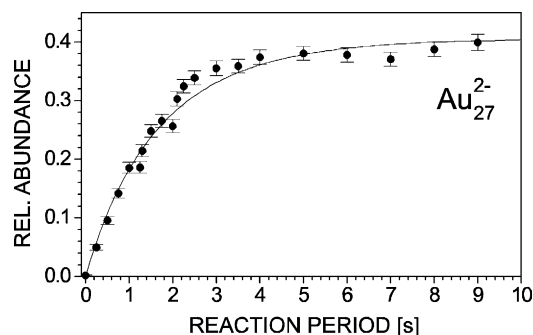


Fig. 2. Relative abundance of gold cluster dianions Au_{27}^{2-} as a function of the reaction period in the electron bath. The solid line is plotted to guide the eye.

of measurements (including the data points from the TOF spectra shown in Fig. 1) all dianions that are produced during the application of the electron beam are ejected out of the trap to avoid a mix-up with dianions that are formed within the reaction period. We note in passing, that it is also possible to eject the electrons from the trap and thus interrupt the charging of the clusters [31].

As Fig. 2 shows, the dianion yield, i.e., the relative abundance of dianions Au_{27}^{2-} , rises within 2 s to about 30% and then levels off for larger reaction periods at 40%. This behavior is consistent with a decrease of the kinetic energy of the stored electrons from the electron bath. As shown in a previous investigation [41], the yield of dianions produced in an electron bath depends on the depth of the trapping potential, presumably because the electrons need sufficient energy to overcome the Coulomb barrier for the attachment to the already charged clusters. Apparently, the electrons lose their energy as a function of time. Possible mechanisms for this energy loss include ion–ion and ion–neutral collisions as well as radiative cooling of the electron motion [42]. A thorough investigation of the relaxation of the kinetic energy of the stored electrons is out of scope of this work. However, the solid line plotted in Fig. 2 suggests a time evolution of the electron attachment that involves an exponential decrease with a typical constant of 0.6 s^{-1} . Thus, the reaction period is chosen to be one second in the following measurements. In addition, the multiply charged clusters formed during the initial 1-s period of application of the electron beam are not ejected in order to increase the number of polyanions and thus the statistical significance of the data.

3. Experimental yields of the dianions and trianions as a function of cluster size

The experimental sequence described above has been applied under the same instrumental conditions to cluster monoanions of different sizes and elements. The noble metals gold, silver and copper have been investigated with respect to the relative yield of their multiply charged anions as produced by electron attachment in the Penning trap. Fig. 3 summarizes the results for the relative dianion yield. For each metal the relative abundances as compared to the monoanionic precursors is plotted as a function of the cluster size. The data points are average values (with the error bar from the uncertainty of the weighted mean) of data from different series of measurements. The solid lines connect the data points to guide the eye. Note, that the data for silver are taken from reference [21]. In case of gold, new measurements have been performed in order to reproduce and extend a previous investigation [19].

The smallest dianions observed are $n = 11$ for gold, $n = 24$ for silver and $n = 32$ for copper. When the respective cluster sizes are increased, the number of dianions increases slowly up to the sizes $n = 19$, 29 and 42 for gold, silver and copper, respectively, where a fast rise in the relative

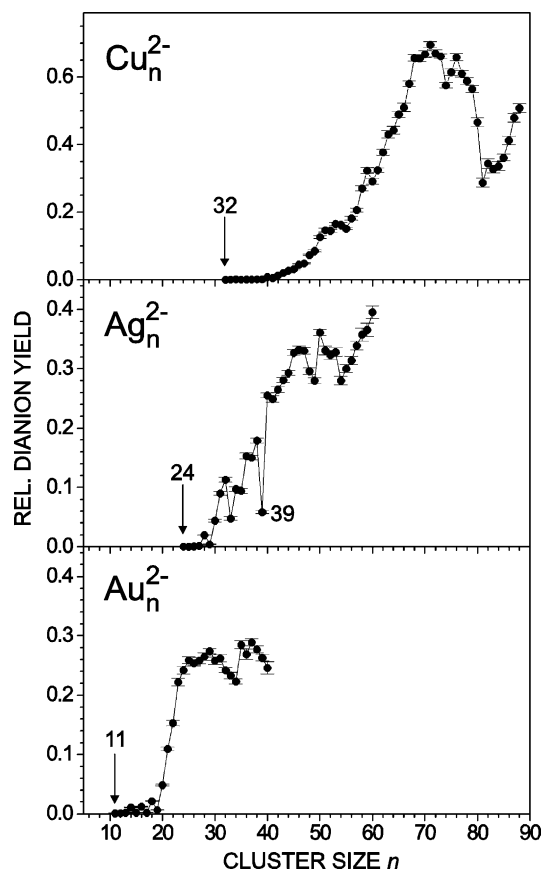


Fig. 3. Relative abundance of gold, silver and copper cluster dianions as a function of the cluster size for a reaction period of one seconds (plus one second for the creation of the electron bath). The data for silver are taken from reference [21].

abundance is observed and at $n = 25$, 50 and 70, the relative yields level off.

On top of the continuous trends of the curves minima of the relative abundance are observed as characteristic structures. For small gold cluster dianions an odd-even staggering is measured that overlaps with a deeper dip at $n = 19$, that is interpreted as an electronic shell closing of the monoanion Au_{19}^- with $n_e = 20$ valence electrons (also see discussion in [19]). At $n = 34$ another minimum is located that possibly belongs to a shell closing with $n_e = 34$ valence electrons, although there is no perfect match ($n = 33$ expected). In case of the silver cluster dianions the electronic structures have already been discussed (see reference [21]). Shell closings are observed for valence electrons $n_e = 30$, 34 and 40. These electronic structures are in good agreement with a theoretical prediction [43].

The minimum at $n = 49$ is identified as an experimental artifact: As mentioned above, a quadrupolar excitation is performed during the application of the electron beam to axialize the cluster monoanions in order to prevent their loss from the trap. By accidental coincidence the excitation frequency ν_c can be twice the axial frequency ν_z of the dianionic clusters, $\nu_c(\text{Ag}_n^{1-}) = 2\nu_z(\text{Ag}_n^{2-})$. Thus, the

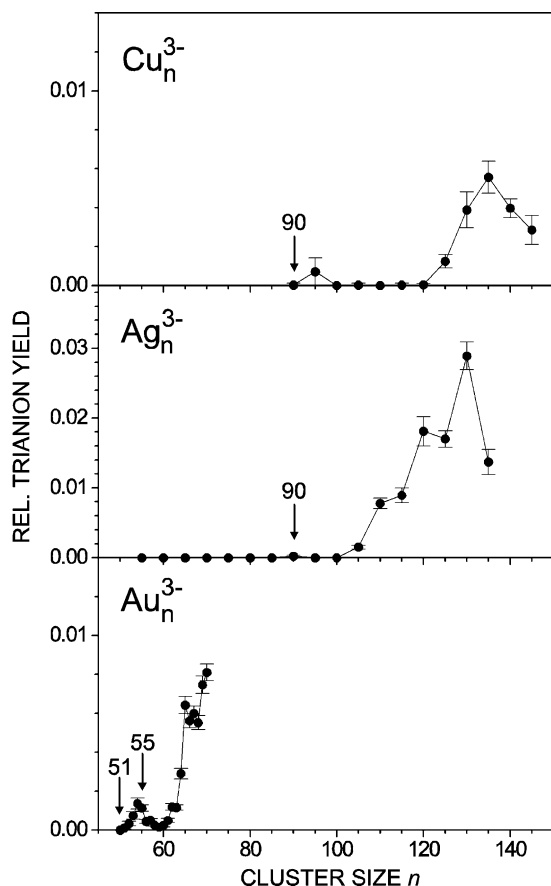


Fig. 4. Relative abundance of trianionic gold, silver and copper clusters as a function of the cluster size (gold data from [20]). The electron bath is applied for one second (with an additional second of reaction time during the creation of the electron bath).

application of the azimuthal quadrupolar excitation (by use of a single-phase rf-signal on two opposed ring segments) leads to a parametric excitation and corresponding growth of the amplitude of the axial motion of the dianions and these clusters are ejected out of the trap [44].

In contrast to the other noble metal clusters, copper cluster dianions show no prominent structures with the exception of a broad minimum at $n = 83$. However, as in the case of $n = 49$ for silver, this feature is explained by a coincidental resonant ejection of dianions out of the Penning trap.

In Fig. 4 the relative abundance of gold, silver and copper cluster trianions is shown as a function of the cluster size. For silver and copper the measurements have been performed in cluster size steps of $\Delta n = 5$. The smallest trianionic gold cluster is observed for $n = 51$. In case of silver and copper the minimal size is $n = 90$.

Gold cluster trianions show a shell closing effect at $n = 55$, i.e., $n_e = 58$ valence electrons, a magic number of the Jellium model, which enhances the stability of the trianions. In contrast, the data for silver and copper do not allow for an interpretation of electronic structures, although earlier observations on cationic silver clusters suggest that at Ag_{55} there may even be a geometric shell closing [37].

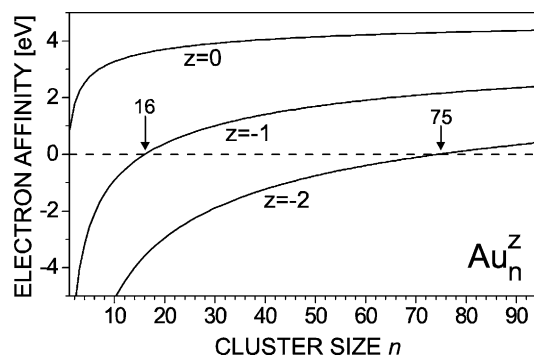


Fig. 5. Electron affinity calculated with a charged sphere model for neutral ($z = 0$), singly ($z = -1$) and doubly charged ($z = -2$) gold cluster anions as a function of the cluster size. The smallest cluster sizes with positive electron affinity are marked with an arrow.

4. Comparison of the experimental onset sizes with the charged sphere model

The observed abundance pattern due to electronic structures as described above have been discussed previously [18–21]. In the following, the interest is focused on the onset of multiply charged noble metal cluster anions. It is analyzed by use of the model of a charged sphere [45,46]. In this model the electron affinity EA, i.e., the amount of energy released in the attachment of an electron to a cluster of charge state z ($z < 0$ for anionic systems) or alternatively the energy needed to detach an electron from a cluster of charge state $z - 1$, can be written as

$$EA = W + ((z - 1) + c) \frac{e^2}{4\pi\epsilon_0(R + \delta)} \quad (1)$$

where W is the bulk work function, δ is a spill-out factor and R is the cluster radius given by

$$R = r_0 n^{1/3} \quad (2)$$

with the Wigner–Seitz-radius r_0 . There has been some controversy about the value of the constant c . For the present study, the classical value of $c = 1/2$ has been adopted [47–49]. In addition, the spill-out δ is an empirical variable, which may also be adjusted. For the following estimations it is neglected, i.e., $\delta = 0$.

The electron affinities for neutral, monoanionic and dianionic gold clusters according to Eq. (1) are plotted in Fig. 5 as a function of the cluster size. The values of r_0 and W taken for the calculation are listed in Table 1. For the work function W the bulk values of several crystallographic directions have been averaged (data taken from [50]).

For negative values of the electron affinity the product anion after electron attachment should not form a stable system. Thus, for gold $n = 16$ and $n = 75$ are expected to be the sizes of the smallest stable dianions and trianions, respectively. The electron affinity is plotted in Fig. 6 as a function of the cluster size for all elements under consideration (for the charge states $z = 0, -1$ and -2). In Table 1,

Table 1

Overview of physical properties of noble metals and threshold sizes for the observation of doubly and triply charged cluster anions (for details, see text)

	Copper	Silver	Gold
Wigner–Seitz-radius (Å)	1.41	1.60	1.59
Work function (eV)	4.64	4.63	5.38
Minimal size for dianions			
Observed	32	24	11
Expected from charged sphere model	36	25	16
Expected with Coulomb barrier	32	22	15
Minimal size for trianions			
Observed	90	90	51
Expected from charged sphere model	167	116	75
Expected with Coulomb barrier	121	84	56

the expected minimal cluster sizes with positive EA for the formation of di- and trianions are listed and compared to the measured values. In case of the dianions the agreement is very good; the difference of a few sizes can be corrected by the implementation of a spill-out factor δ , a different value for the constant c or adjustments of the work function and the cluster radius. These parameters have been taken from the bulk properties and small deviations for the quantum size regime are not surprising.

The trianion cluster sizes are larger and thus their properties should be even closer to the bulk. However, for the trianions the difference between the observed values and those predicted by the charged sphere model are much larger and cannot be adjusted by minor correction to the parameters. The expected minimal sizes are 24–77 units above the observed values.

In order to get a better match, similar to the case of the dianions, the repulsive Coulomb barrier has to be taken into account. For multianions with negative electron affinity the Coulomb barrier prevents the immediate electron detachment which thus can proceed by tunneling only. From classical electrostatics [51], the Coulomb barrier for electron attachment onto a spherical metal cluster of charge state z ($z < 0$) and radius R is given by

$$V_C(r) = \frac{e^2}{4\pi\epsilon_0 R} \left(\frac{|z| R}{r} + \frac{R^2}{2r^2} - \frac{1}{2} \frac{R^2}{(r^2 - R^2)} \right) \quad (3)$$

where the polarizability (i.e., the influence of image charges) has been included. For the attachment to monoanions, $z = -1$, or for the detachment from dianions, the height of the Coulomb barrier amounts to

$$V_{C,\max} = \frac{e^2}{8\pi\epsilon_0 R} \quad (4)$$

which is located at a distance

$$r_{C,\max} = \frac{1}{2}(\sqrt{5} + 1)R \quad (5)$$

from the cluster center [19]. For higher charge states ($z < -1$) the barrier heights and its position have been obtained numerically. As an example, Fig. 7 shows the Coulomb barrier of Au_{14}^- calculated with Eq. (3), where the energy of the excess electron of the dianion is plotted with a dashed line.

Adding the Coulomb barrier height $V_{C,\max}$ to the electron affinity (see dashed lines in Fig. 6) leads to a shift to smaller sizes of the expected observable polyanions. But in order to have a measure of the influence of the Coulomb barrier on

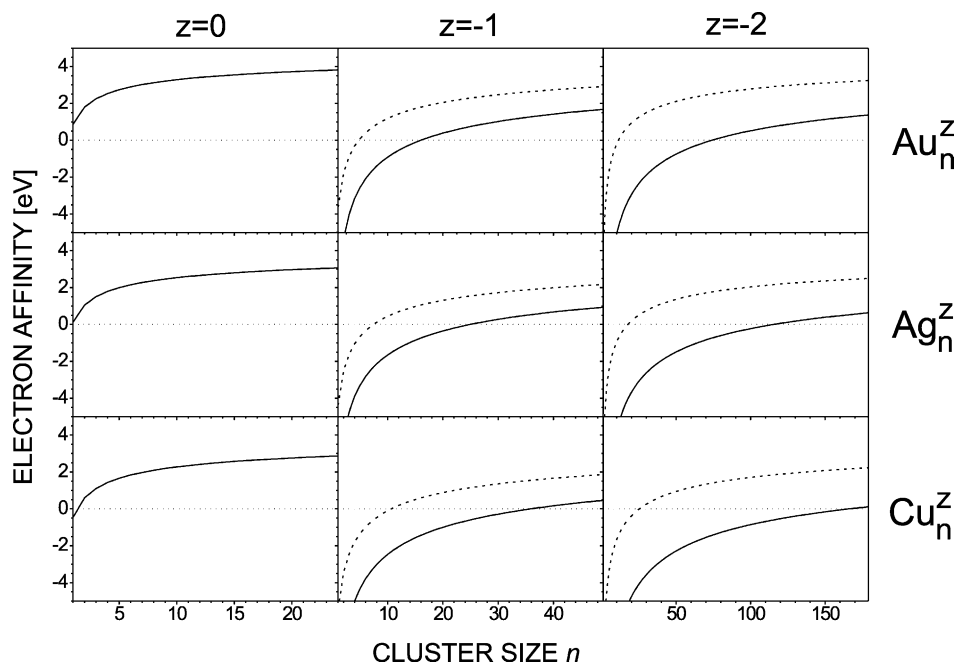


Fig. 6. Electron affinity (solid line) of neutral ($z = 0$), singly ($z = -1$) and doubly charged ($z = -2$) gold, silver and copper cluster anions as a function of the cluster size as calculated with Eq. (1). The dashed lines represent the sum of the electron affinity and the maximum of the Coulomb barrier (Eq. (4)).

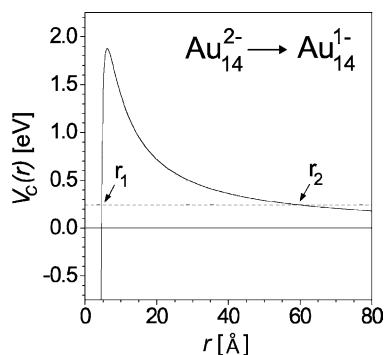


Fig. 7. Coulomb barrier calculated with Eq. (3) for the monoanion Au_{14}^{2-} (solid line). The dashed line indicates the energy of the surplus electron of the dianion.

the (meta)stability of the anions, the tunneling of a surplus electron has to be investigated as shown for dianionic systems by Wang and coworkers [8,52]. The probability for the tunneling is calculated by use of the WKB approximation [53]:

$$P = \exp\left(-\frac{2}{\hbar} \int_{r_1}^{r_2} \sqrt{2m(V_C(r) - E)} dr\right) \quad (6)$$

with E as the absolute value of the (negative) electron affinity and the electron mass m . The lifetime τ , i.e., the average time the electron stays inside the cluster is calculated by

$$\tau = \frac{2r_1}{v} \frac{1}{P} \quad (7)$$

where $v = \sqrt{2E/m}$ is the velocity of the electron.

The lifetimes τ for dianions and trianions of copper, silver and gold clusters with negative EA are plotted in Figs. 8 and 9, respectively (values larger than 10^{30} s have been set to 10^{30} s and marked with open symbols). Since the experimental reaction period (for attachment) has been set to one second, cluster sizes with lifetimes of about one second and longer live long enough in order to be observed in the experiment. With this definition, the minimal sizes as listed in Table 1 agree very good with the observed values. Note, that the effect of the Coulomb barrier is much stronger in the case of the trianions than for the dianions.

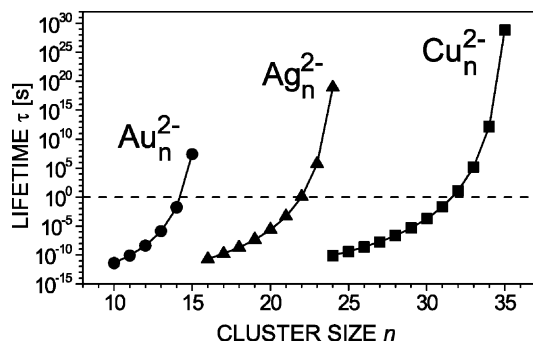


Fig. 8. Lifetimes of gold, silver and copper cluster dianions with $\text{EA} < 0$ as a function of the cluster size, as calculated by numerically solving Eq. (7).

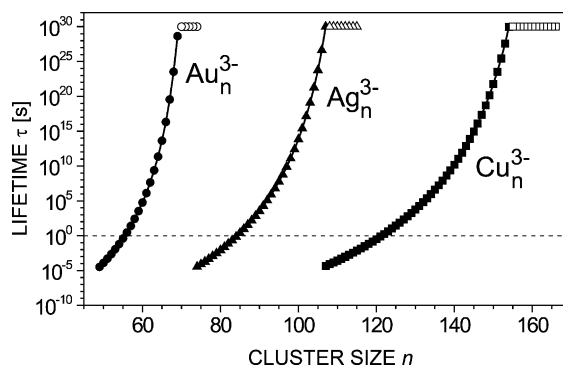


Fig. 9. Lifetimes of gold, silver and copper cluster trianions with $\text{EA} < 0$ as a function of the cluster size, as calculated by numerically solving Eq. (7). Data points with $\tau > 10^{30}$ s are marked with open symbols.

In all cases the observed relative yields are influenced by the attachment probability, which depends on the properties of the electrons from the electron bath but also on the electron affinity and the Coulomb barrier of the anion to be charged. All these factors add up and result in the observations shown in Figs. 3 and 4. Thus, the electron affinity, approximated with Eq. (1), cannot be directly tested, in particular if the roughness of the estimation of the parameters W , r_0 , c and δ is also taken into account. In addition, a finite thermal energy of the clusters, as in the present case, is expected to lead to a decrease of the corresponding lifetimes. However, this effect is not easily estimated for several reasons: The heating of the anions by direct collisions with the primary electrons is not known; neither is the energy imposed by the absorption of further electrons; and the coupling between the electronic and vibrational degrees of freedom is another source of uncertainty. Thus, for the current study, the effect of finite thermal energy has been neglected. Nevertheless, as shown above, a qualitative interpretation of the smallest sizes observed can be derived.

The explicit time dependence of the decay of metastable states has not yet been observed. However, in principle, it should be possible to measure the lifetimes of long-lived multianions: The Penning trap allows extended storage times of up to several seconds or longer and therefore the decay of a polyanion by electron autodetachment should be measurable time-resolved, especially since the products are still charged and can be detected. From such lifetimes the energy of the emitted electron before the tunneling process could be calculated, as shown by Kappes [15] and coworkers in case of metastable platinum-tetrahalide-dianions.

5. Conclusion and outlook

Dianionic and trianionic noble metal clusters have been produced by bathing monoanions in simultaneously stored electrons in a Penning trap. The onset sizes for observation of multiply charged cluster anions have been determined. They can be explained with a charged sphere model where

the repulsive Coulomb barrier prevents autodetachment of electrons from systems with negative electron affinity on the timescale of seconds. To further investigate the properties of multiply charged metal cluster anions, lifetime measurements of metastable polyanions are in preparation in addition to photoexcitation experiments.

Within the charged sphere model it is possible to predict the EA of the next charge state ($z = -3$), i.e., the appearance size of quadruply charged metal cluster anions. The smallest trianion cluster sizes with a positive electron affinity are $n = 204$, 317 and 456 for gold, silver and copper, respectively. When the Coulomb barrier and tunneling processes are included the appearance sizes are shifted to $n = 128$, 193 and 278. With the current setup anionic gold clusters as heavy as Au_{145}^- have already been captured and stored [54], i.e., the expected onset sizes are within reach.

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