Two-electron emission after photoexcitation of metal-cluster dianions

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Abstract. Size-selected metal-cluster dianions of the elements gold, silver and copper have been photoexcited by nanosecond-pulse and continuous laser irradiation, which leads to electron emission and monomer evaporation. In addition to the observation of these competing decay pathways, there is a reduction of the total cluster-ion intensity, which indicates the neutralization of dianions, i.e. the loss of both surplus electrons. In contrast, the activation of singly charged anionic clusters of the same type results primarily in dissociation by monomer evaporation and not by electron emission. These decay processes as observed for doubly and singly charged cluster anions suggest that the dianions emit two electrons simultaneously, i.e. in a correlated fashion. A classical conducting-sphere approximation confirms that the Coulomb barrier for symmetric two-electron emission is lower than the Coulomb barrier for the emission of a single electron.

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Multiply charged many-particle systems are encountered on various length scales ranging from atomic nuclei up to macroscopic droplets. Immediately after the question of how much charge such a system can carry, or (considered from a slightly different point of view) how large the system has to be to stably hold a given amount of electrical charge, follows the question of how the system breaks apart either if the charge exceeds this limit or if the system is excited.

For nuclei, fission, alpha and proton decays are well-known processes; in the latter case two-proton emission has recently drawn much attention [1, 2]. On the micrometer scale, highly charged micrometer-sized droplets of ethylene glycol show Coulomb fission by the emission of low-mass highly charged jets when their size is reduced below the Rayleigh criterion [3, 4]. At the low-size end of the droplets, multiply charged metal-cluster cations were investigated thoroughly during the 1980s and 1990s. For these systems the Coulomb instability was found to typically lead to asymmetric fission as reviewed by Näher et al [5]. For excited clusters this decay path competes with the evaporation of neutral atoms.

In the meantime, the field of multiply charged metal clusters has been extended by the introduction of methods for producing higher negative charge states for metal clusters, in particular by the technique of ‘electron bathing’ in Penning traps [6–8]. Several investigations have been performed, mostly with respect to the production of such species [9–12], but also with respect to their stability and decay pathways [13, 14]. While the charge-state reduction of cations is always accompanied by the loss of one or several atoms (for monovalent metals,
Table 1. LDM parameters for the elements gold, silver and copper as used in this work. Data are taken from [16, 24, 25].

| Element | $R_a$ (10$^{-10}$ m) | $a_V$ (eV) | $a_S$ (eV) | $a_C$ (eV) | $W$ (eV) |
|---------|----------------------|------------|------------|------------|----------|
| Au      | 1.59                 | 3.81       | 3.00       | 4.52       | 5.38     |
| Ag      | 1.60                 | 2.95       | 2.50       | 4.51       | 4.63     |
| Cu      | 1.41                 | 3.49       | 2.80       | 5.10       | 4.64     |

usually a trimer [15], but sometimes also atomic ions, i.e. the above-mentioned fission), anions have the alternative to emit electrons.

In this work, the possible decay-pathway options of doubly charged anionic metal clusters are reviewed in the framework of the liquid-drop model (LDM) and the conducting-sphere approximation: monomer evaporation, fission and electron emission. Experiments on size- and charge-state-selected coinage metal-cluster dianions have been carried out by the use of a Penning trap. The stored dianions were subjected to photons from either a pulsed or a continuous laser beam and the products were analyzed with respect to the aforementioned decay pathways.

Most notably, the experimental findings include a loss of the total cluster-ion signal, which indicates the emission of two instead of only one electron. As experiments with the photoexcitation of singly charged cluster anions do not show the corresponding ion loss, it can be concluded that the two-electron emission is not simply a sequential process, but instead the two electrons are emitted simultaneously. These findings are discussed in the framework of the LDM for symmetric emission of the two surplus electrons of the dianions. Indeed, it is found that the Coulomb barrier of the simultaneous two-electron emission is significantly reduced with respect to the emission of a single electron.

2. Considerations on possible decay mechanisms

2.1. Liquid-drop model of metal clusters

In the following, the possible decay modes of metal dianions are reviewed in the framework of the LDM [16–19] and conducting-sphere approximation. The cluster volume is assumed to be the sum of the volumes of the $n$ atomic constituents. Thus, the radius of the cluster is given by

$$R(n) = R_an^{1/3}$$

and its surface by

$$S(n) = 4\pi R_a^2n^{2/3}.$$  

By taking the difference of the total energy of the cluster precursors and the possible reaction products and adding Coulomb barriers where applicable, the decay pathways can be compared with respect to the minimal energies required.

The total energy of a cluster of $n$ atoms and charge state $z$ (with $z = -1$ for monoanions and $z = -2$ for dianions) is approximated by the sum

$$E(n, z) = -a_Vn + a_Sn^{2/3} + a_Cz^2n^{-1/3} + zW.$$  

The first term of this expression is the volume energy, where $a_V$ is the average binding energy of an atom in the bulk (for the values of the coefficients of the present elements, see table 1). The
surface-energy term has a coefficient $a_S = 4\pi R_a^2 \sigma$, where $\sigma$ is the surface tension. The last two terms describe the additional Coulomb energy with the coefficient $a_C = e^2 / (8\pi \varepsilon_0 R_a)$ [20] and the workfunction $W$ released for each additional electron attached. Note that in the notation of equation (3) all coefficients as well as the workfunction have a positive value. Thus the volume term is negative, the surface and the Coulomb terms are positive (independent of the sign of the charge state) and the workfunction term is negative for anionic species ($z < 0$). The total energy of bound systems has a negative value. Changing the sign gives the total binding energy.

2.2. Neutral monomer evaporation

In general, there are several competing decay pathways of coinage metal clusters $M_n^z$ of size $n$ and charge state $z$. First, they may dissociate via the emission of neutral fragments, in particular single atoms, i.e. neutral monomer evaporation,

$$M_n^z \rightarrow M_{n-1}^z + M.$$ \hfill (4)

In addition, dimer evaporation $M_n^z \rightarrow M_{n-2}^z + M_2$ has been observed (see, e.g., [21]), but only in the case of rather small cluster systems, which will not be considered in the following.

The dissociation energies for monomer evaporation,

$$D(n, z) = E(n - 1, z) - E(n, z) \hfill (5)$$

$$= a_V + a_S((n - 1)^{2/3} - n^{2/3}) + a_Cz^2((n - 1)^{-1/3} - n^{-1/3}), \hfill (6)$$

are shown as solid lines in figure 1 for (a) gold, (b) silver and (c) copper clusters as a function of the cluster size. Note that although the clusters emit neutral atoms, the dissociation energy is a function of the charge state, as the change in the size of a cluster results in a change in its Coulomb energy. This effect is particularly large for small clusters.

2.3. Fission of dianions

In the case of multiply charged clusters the charge may be split between the products. For doubly charged clusters this results in the dissociation

$$M_n^{\pm} \rightarrow M_{n-m}^{\pm} + M_m^{\pm}, \hfill (7)$$

where $m$ can vary between $m = 1$ and $m = n/2 \ (m = n - 1, n - 2, \ldots \text{ leads to the same reactions as } m = 1, m = 2, \ldots)$. Such processes, which are usually called fission, have been observed several times for coinage metal cluster cations, in particular with the ClusterTrap apparatus [22, 23]. In order to initiate this unimolecular dissociation, not only the difference of total energy between products and precursor, in the context of fission often called $Q$ value and for dianions given by

$$Q_i(n, m) = E(n - m, z = -1) + E(m, z = -1) - E(n, z = -2), \hfill (8)$$

but also a Coulomb barrier has to be overcome. The fission processes of metal clusters have been reviewed in detail by Näher et al [5]: similar to the fission of atomic nuclei, a fission parameter can be defined [5] as the Coulomb energy over twice the surface energy:

$$x(n, z) = \frac{a_C}{2a_S} \frac{z^2}{n}. \hfill (9)$$
Figure 1. Dissociation energy as a function of the cluster size $n$ (solid line), the second electron affinity (dash-dotted line) and the second electron affinity with added Coulomb barrier height, i.e. activation energy for electron emission (dashed line) for (a) gold, (b) silver and (c) copper clusters. (d) For comparison the minimum fission barrier (empty symbols) and symmetric fission barrier (filled symbols) as a function of the cluster size (for gold) are shown.

For $x(n, z) \geq 1$ the fission proceeds spontaneously, whereas for $x(n, z) < 1$ an activation energy is required for deformation until fission is achieved. The potential barriers $V_f(n, m)$ due to the Coulomb repulsion can be estimated in the framework of the ‘touching-sphere model’ by the electric potential of the two fragments $M_{n-m}^1$ and $M_m^1$ in the moment of breakup (or touching for the reverse process). The shapes are, again, approximated by spheres. The present calculations, including the mutual polarization, have been performed as outlined in detail by Krückeberg et al (see [22] and references therein). The fission barrier is thus given by

$$D_f(n, m) = Q_f(n, m) + V_f(n, m).$$

(10)

The fission barrier is not uniquely determined by the size of the precursor dianion but also depends on the ratio of the size of the two product clusters ($m$ and $n - m$). Figure 1(d) displays...
the values of $D_f(n, m)$ for $\text{Au}_n^{2-}$ as a function of cluster size for the case of symmetric fission ($m = n/2$ for even $n$ and $m = (n \pm 1)/2$ for odd $n$) as well as for the size ratio with the lowest barrier (in general, highly asymmetric is energetically favored to symmetric fission). Obviously, the activation energy needed for fission is much higher than that of neutral monomer evaporation (solid line) and electron emission (dashed line, discussed below). Note that gold cluster dianions have been observed to exist for sizes $n \geq 12$ only [7]. Therefore, fission will be excluded in the following.

2.4. Electron emission

While evaporation of neutral parts and fission into two charged particles are the only possible decay pathways of dicationic clusters, there is an additional possible decay mode in the case of dianions, namely electron emission:

$$M_n^{2-} \rightarrow M_n^{1-} + e^-.$$ (11)

As in the case of fission, both the change of energy as well as the Coulomb barrier have to be taken into account for this process. According to equation (3) the energy balance for the change from charge state $z = -2$ to $z = -1$ is given by

$$Q_e(n) = E(n, z = -1) - E(n, z = -2)$$

$$= W - 3a_C n^{-1/3}. \quad \text{(12)}$$

The energy $Q_e(n)$ is the ionization potential, i.e. the energy needed to remove an electron from the dianionic system, or from another point of view, the electron affinity of the monoanionic cluster, i.e. the energy released in the reverse reaction of electron attachment. In fact, $Q_e(n) = 0$ marks the limit of stable dianionic clusters. In figure 1, the dashed-dotted lines show these electron ionization energies/affinities for (a) gold, (b) silver and (c) copper clusters as a function of cluster size. The crossing with the $x$-axis indicates the corresponding appearance sizes for gold, silver and copper cluster dianions in good agreement with the experimental findings [12, 26].

In addition, the Coulomb barrier plays an important role in the attachment of surplus electrons [27]. Furthermore, it has to be taken into account for the electron emission process, since the electron has to overcome the barrier. The Coulomb barrier height for the attachment of a second surplus electron to a monoanion and thus also for the detachment of a surplus electron from a dianionic cluster is given by [12]

$$V_C(n) = a_C n^{-1/3}. \quad \text{(13)}$$

In total, the activation energy for electron emission is thus given by

$$D_e(n) = Q_e(n) + V_C(n) = W - 2a_C n^{-1/3}, \quad \text{(15)}$$

which is shown as dashed lines in figure 1. Note that in contrast to the case of fission the electron emission leads to a unique value for $D_e(n)$. For small clusters this value is considerably below the energy $D(n, z)$ for neutral monomer evaporation, whereas for the larger clusters the situation is reversed. The crossing of the curves occurs at the cluster sizes $n \approx 92, 86$ and 383 for gold, silver and copper, respectively.

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2.5. Conclusion on expected decay pathways

While there are in principle three possible decay modes for dianionic coinage metal clusters, one of them, namely fission into two monoanionic pieces, can be removed from the expected observations, at least for the present case of size-range and moderate excitation energies. For small clusters electron emission seems energetically favored, whereas for larger cluster sizes, neutral-monomer evaporation is the expected decay pathway.

2.6. Calculation of decay rates

The cluster decays happen as the result of statistical processes. The decay rate depends on the thermodynamical cluster properties and the energy of the precursor. In the present work, the Weisskopf formalism is applied (see [13] and references therein), which results in a decay rate

\[ k(E, E_B) = \frac{2m}{\pi^2 \hbar^2} \sigma_c k_B^2 T_D \rho_D (E - E_B) \rho_P(E), \]

where \( E \) is the energy of the cluster and \( E_B \) the binding energy of the electron or the monomer. The cross-section \( \sigma_c \) is taken from the reverse process of capturing an electron or a monomer and \( m \) is either the mass of the electron or the reduced mass in the case of monomer evaporation. \( T_D \) is the temperature of the daughter system and \( \rho_D \) and \( \rho_P \) are the level densities of the daughter and parent system, respectively. In the case of dianionic gold clusters this decay-rate model has been used to describe thermionic electron emission after photoexcitation of Au\(_{29}^2^-\) [13] and electron emission from gold-cluster dianions after collisional activation [14]. In addition, monomer evaporation from anionic gold clusters was described using this approach [28]. The resulting monomer dissociation energies and electron binding energies were comparable to the expected LDM values and in reasonable agreement with those extrapolated from cationic cluster data [13, 14, 28]. Therefore, the decay rates as given by equation (16) can be assumed to provide useful estimates for the decay processes studied in this work (single-electron emission and monomer evaporation).

3. Experimental setup and procedure

The experimental setup has been described in detail elsewhere [29]. The ClusterTrap experiment consists of a cluster ion source, a Penning trap with hyperbolic electrodes superimposed by a homogeneous 5 T magnetic field and a time-of-flight (ToF) mass-spectrometry section. Singly charged clusters are produced by laser vaporization from a metal wire, subsequent cooling with a helium gas pulse and adiabatic expansion into vacuum [30]. The anions are guided by ion-optical elements to the Penning trap where they are captured in-flight [31]. It is also possible to accumulate several ion bunches from the ion source [32] using a buffer-gas cooling technique [33]. The stored ions can be size-selected by mass-selective excitation of the cyclotron motion of the unwanted ions, i.e. by radially ejecting them from the trap by the use of a dipolar rf excitation. After these preparatory steps, further experimental procedures can be performed while the ions are stored in the trap. The ion ensemble resulting after each step can be analyzed by ejection of all ions into a ToF drift section and detection by a combination of a conversion electrode and a micro-channel plate detector. This detector arrangement allows line-of-sight
access of laser beams along the symmetry axis of the Penning trap through the central bores in the endcaps through which the clusters are injected and ejected, too.

3.1. Dianion formation

The experimental sequence as applied in the present work is shown schematically in figure 2(a). For the production of dianions, an electron bath of low-energy electrons is created by ionizing argon atoms with an electron beam that is guided by the magnetic field from an external source through the center of the Penning trap [12]. The secondary electrons are stored together with the cluster anions and during a few hundreds of milliseconds up to a few seconds dianionic clusters are formed by their attachment. The monoanions that have not captured an additional electron are removed from the trap by the use of a dipolar rf excitation as applied earlier in the cycle for mass-selection (at an appropriate excitation frequency). Thus this second application is used for charge-selection. Before photoexcitation, the dianions are thermalized by buffer-gas collisions and in combination with a quadrupolar rf excitation a centering of the ions is performed [33] to ensure reproducible initial conditions. Furthermore, the electron bath is removed by pulsing down the potential of one end-cap electrode of the Penning trap (suspended trapping [34, 35]) prior to photoexcitation. In general, the pressure in the trap region is below $1 \times 10^{-8}$ mbar and the buffer gas, which is pulsed into the trap volume, is rapidly pumped away to ensure ultrahigh vacuum conditions. Usually, the same experimental cycle was repeated in alternation without photoexcitation in order to account for fluctuations in the cluster and dianion production, i.e. relative abundances rather than absolute cluster yields have been monitored.

3.2. Photoexcitation

After dianion production and centering in the Penning trap, the stored dianions were photoexcited by a 10 ns pulse of an Nd:YAG laser. The pulse energy of the third harmonic ($\lambda = 355$ nm, $E_{ph} = 3.49$ eV) was varied by adjusting the $Q$-switch of the Nd:YAG laser and monitored by measuring the intensity of the low-energy pulse from a 5% beam splitter. For
this work, the reaction duration, i.e. the delay between the laser pulse and the product analysis, was kept constant at $T_R = 100$ ms. Alternatively, a continuous irradiation at $\lambda = 532$ nm was performed.

The experimental sequence is illustrated in figure 2(b) by abundance spectra taken after the main steps (from top to bottom): size selection of gold cluster anions (here Au$_{28}^{-}$), application of an electron bath for dianion production, charge selection (of Au$_{28}^{2-}$) by radial ejection of the monoanionic clusters and photoexcitation by the laser pulse (in this case of pulse energy 1 mJ).

The photoexcitation of clusters stored in the Penning trap has already been discussed in detail elsewhere [37, 38]. In the most simple case of a homogeneous laser beam profile with full spatial overlap with the ensemble of initially $N_A$ clusters (as can be assumed for the pulsed excitation in this work), the number of precursors that have not yet absorbed any photon after the laser pulse of duration $T$ is given by

$$N_0(\rho, T) = N_A \exp(-\sigma \rho T),$$

(17)

where $\rho$ is the photon flux density and $\sigma$ the absorption cross-section. Thus, the number of clusters that have absorbed at least one photon is given by

$$N_{\geq 1}(\rho, T) = N_A(1 - \exp(-\sigma \rho T)).$$

(18)

However, not all reactions may occur after the absorption of just one photon. If another photon is needed, then the corresponding considerations lead to

$$N_{\leq 2}(\rho, T) = N_A(1 + \sigma \rho T) \exp(-\sigma \rho T)$$

(19)

systems that have not yet absorbed more than one photon and

$$N_{\geq 2}(\rho, T) = N_A(1 - (1 + \sigma \rho T) \exp(-\sigma \rho T))$$

(20)

clusters that have absorbed at least two photons.

For the experiments with continuous laser irradiation the condition of full spatial overlap was fulfilled. Nevertheless, a homogeneous photon flux, as estimated for the pulsed photoexcitation, was not achieved. However, both the laser profile (as measured with a CCD camera, see figure 3) and the cluster-ion distribution can be approximated by Gaussian shapes [37], which allow one to calculate the convolution to determine the corresponding number of clusters that absorbed zero, one or more and two or more photons.

4. Experimental results and discussion

4.1. Decay pathway competition between monomer evaporation and electron emission

In a first sequence of experiments gold-cluster dianions Au$_n^{2-}$, $n = 35, 40, 45, 50$, have been photoexcited with a relatively high laser-pulse energy of about 20 mJ. The resulting abundance spectra are shown in figure 4(a). In all cases signals are observed at twice the value of the mass-to-charge ratio, i.e. twice the cluster size-to-charge ratio $n/z$. These are due to monoanions produced by electron emission of the dianionic precursors. Because of the high laser-pulse energy and thus the large number of absorbed photons, the monoanionic clusters further decay by sequential monomer evaporation and create a chain of signals at smaller cluster sizes. Note that for the precursor cluster sizes $n = 35$ and $n = 40$ a noticeable dip of the signal intensity at Au$_{34}^{-}$ is observed. This behavior is in accordance with the reduced stability of Au$_{34}^{-}$ as this cluster of a monovalent element has a single electron beyond the ‘magic number’ 34 known...
Figure 3. Profile of (a) the pulsed Nd:YAG laser ($\lambda = 355$ nm) and (b) the continuous Nd:YAG laser ($\lambda = 532$ nm) measured with a CCD camera. The CCD camera array was positioned at the same distance as the center of the Penning trap relative to the lasers. (c) Cut through the Penning trap electrodes.

as an electronic subshell [39, 40]. Such shell-structure phenomena are beyond the scope of the present study and will therefore not be further considered in this work.

In addition to the appearance of monoanions and their decay chains, decay chains are also observed for the precursors themselves, i.e. the gold cluster dianions. Apparently, the dianions may also decay by sequential fragmentation. However, there is a clear size dependence: while the larger clusters, $\text{Au}_{45}^{2-}$ and $\text{Au}_{50}^{2-}$, show significant amounts of dianion products, there are only a few in the case of $\text{Au}_{40}^{2-}$ and almost none for $\text{Au}_{35}^{2-}$. Obviously, there is a tendency toward neutral-monomer evaporation with increasing cluster size, which competes with electron emission as a decay pathway. Note that the attachment of electrons after fragmentation of monoanionic product clusters is highly unlikely as the electron bath has been removed prior to photoexcitation (see ‘pulse endcap’ in figure 2(a)).

In order to interpret the size dependence of the decay branching ratio, the dissociation energy (for neutral-monomer evaporation) and the activation energy for electron emission of gold clusters are compared (see figure 1(a)). The dissociation energy is almost constant in the mass range $10 \leq n \leq 150$, while the activation energy for electron emission increases and crosses the curve of the dissociation energy at about $n \approx 90$. This explains the competition between monomer evaporation and electron emission as observed for gold-cluster dianions in the experiment.

In the case of copper-cluster dianions, electron emission is observed, too (see figure 4(b) for an abundance spectrum after photoexcitation of $\text{Cu}_{70}^{2-}$). However, monomer evaporation for
Figure 4. Abundance spectra recorded after photoexcitation of size- and charge-state-selected $\text{Au}_n^{2-}$, $n = 35, 40, 45, 50$, and $\text{Cu}_{70}^{2-}$.

dianions in this size range seems to be suppressed according to the difference in dissociation energy and activation energy for electron emission as shown in figure 1(c).

After these initial experiments the laser-pulse energy was reduced for a systematic study of the first decay steps. The laser-pulse energy was varied between 4 and 7 mJ and the width of the laser profile was increased to obtain an almost homogeneous photon flux for the stored cluster ions. Figure 5 shows the resulting ratio of the abundance of doubly charged products (following monomer evaporation) and singly charged products (following electron emission) as a function of the gold-cluster size.

The rates for monomer evaporation and electron emission are given by the Weisskopf formalism as defined in equation (16). The resulting expected decay-rate ratio after absorption of 1, 2, 3 and 4 photons is shown in figure 5. The general trend of increased neutral monomer evaporation for larger dianionic precursors versus increased electron emission for smaller precursors is reproduced. In addition, two-photon absorption agrees best with the experimental data points.
**Figure 5.** Abundance ratio as a function of cluster size of the observed doubly and singly charged product gold-clusters after photoexcitation. The solid lines are calculated ratios of decay rates for monomer evaporation and electron emission after absorption of 1, 2, 3 or 4 photons of $E = 3.49 \text{ eV}$.

**Figure 6.** Relative abundance of (a) dianionic products and (b) monoanionic products after photoexcitation of Au$_{45}^{2-}$ as a function of the laser-pulse energy. The solid line is a fit to the data for the absorption of at least one photon, while the dashed line is a fit to the data for the absorption of at least two photons.

The question of the number of absorbed photons that are responsible for the decay processes has been further investigated for the case of Au$_{45}^{2-}$, i.e. a cluster size where the probabilities of electron emission and neutral monomer evaporation are similar. The intensity of the products of both processes has been monitored as a function of the laser-pulse energy (see figure 6). The solid and dashed lines in figure 6 are linear and quadratic fits to the data points under the assumption of one-photon and two-photon absorption, respectively, as expected from Taylor expansions of equations (18) and (20) in the limit of small photon fluxes.
These results seem to indicate that neutral monomer evaporation requires the absorption of at least two photons of $E_{ph} = 3.49$ eV, while in the case of electron emission one photon is sufficient. However, this would be in sharp contradiction to the decay-rate values expected in the Weisskopf formalism for one-photon and two-photon processes (as calculated using the procedure of [13]): while the electron emission for the smaller cluster di-anion $\text{Au}_{29}^-$ after activation by $2 \times 3.49$ eV (and the initial thermal energy at room temperature, $T = 300$ K) is expected at a decay rate of $38 \text{s}^{-1}$, the corresponding electron-emission rate for $\text{Au}_{45}^-$ is only $7 \times 10^{-6} \text{s}^{-1}$, and for monomer evaporation $4 \times 10^{-6} \text{s}^{-1}$, i.e. both processes are similar (as observed, see again figure 5) but unlikely in the time window of the present investigations ($T_R = 100 \text{ms}$). The rate for electron emission of $\text{Au}_{45}^-$ after absorption of one photon is several orders of magnitude smaller, i.e. no electron emission should occur. In summary, the dependence of the product intensity on the laser-pulse energy does not lead to a conclusive assignment of the absorbed number of photons (reminding us of earlier findings for the neutral monomer evaporation of gold-cluster monocations [41, 42]).

4.2. Loss of gold-cluster anions after pulsed photoexcitation

Up to here, only the individual relative abundances of the mono- and di-anionic products resulting from the photoactivation have been considered as well as their ratio. In addition, the ToF spectra show the remaining precursor di-anions. This additional information as well as that of the experimental reference cycles has also been further evaluated. As an example, figure 7(a) shows the spectra of $\text{Au}_{30}^-$ before (top) and after (bottom) irradiation with a $22 \text{mJ}$ laser pulse. Note first that there is no indication of a di-anionic product cluster, such as $\text{Au}_{29}^-$ or $\text{Au}_{28}^-$. This is in accordance with our expectations from the trend in figure 4(a). In addition, as both spectra are normalized to the reference spectrum (i.e. the top spectrum without photoexcitation), it is found that obviously a significant number of clusters are ‘lost’. 

Ion loss has been observed in earlier measurements where the collisional activation of di-anions has been studied [14]. In these experiments the ion loss was due to a technical feature, namely a sudden change of the ion trajectory in the Penning trap as the emission of an electron marked a sudden change of the charge state and thus in cyclotron frequency [43]. To initiate the collisions with buffer-gas atoms, the ions were brought to a large cyclotron radius, which increases significantly after electron emission [43]. As a result, the radial ion trajectory exceeds the trap dimensions and the product ions are lost, either immediately by collision with the ring electrode or during the axial ejection, as they hit the end-cap electrode (with a diameter of the central bore of only $5 \text{mm}$). In contrast, in the case of photoexcitation the cluster di-anions remain centered in the trap. Thus the ion position is not influenced by electron emission (the recoil is negligible) and no clusters are lost during ejection of the ions toward the ToF drift tube and detector.

However, as the Penning trap stores only charged particles, only the di- and mono-anionic clusters are further trapped and finally detected. If the di-anionic precursors lose both of their surplus electrons and are thus neutralized, the clusters are immediately lost from the trap. In the absence of another explanation (in contrast to the case of collisional activation mentioned above) it is therefore concluded that two electrons are emitted to explain the disappearance of the missing clusters.

In the example shown in figure 7(a) the laser-pulse energy is rather large ($22 \text{mJ}$) and thus leads to sequential decay of the few mono-anionic primary product ions. In order to further check
Figure 7. (a) Abundance spectra of Au\(_{30}^{2-}\) without (top) and after photoexcitation (bottom) at a laser-pulse energy of 22 mJ. (b) Relative abundance of Au\(_{30}^{2-}\) and products Au\(_n^{1-}\) as a function of the laser-pulse energy. The gray-shaded band shows the sum of the two relative abundances as 1\(\sigma\)-uncertainty band. (c) Abundance spectra of Au\(_{30}^{1-}\) without (top) and after photoexcitation (bottom) at a laser-pulse energy of 22 mJ. (d) Relative abundance of Au\(_{30}^{1-}\) and products Au\(_n^{1-}\), \(n < 30\), as a function of the laser-pulse energy. The gray-shaded band shows the sum of the two relative abundances as 1\(\sigma\)-uncertainty band.

The behavior of the product clusters (all singly charged, as already noted above) as well as the doubly charged precursor cluster, the laser-pulse energy was varied systematically. As shown in figure 7(b) the relative abundance of dianions decreases exponentially down to just a few percent but the relative abundance of singly charged product clusters (empty circles) only reaches 20–30%. The gray-shaded band (1\(\sigma\)-uncertainty band) gives the relative abundance of all cluster anions observed after photoexcitation which is essentially composed of singly charged products at high laser-pulse energies. Clearly, a loss of ions is observed, i.e. up to about 80% of the product clusters are not detected after photoexcitation. This loss is explained by the creation of neutral clusters.

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In principle, the ion loss could be due to monoanionic product clusters performing electron emission in competition with neutral monomer evaporation. On their way to the neutral charge state, the dianions could lose the two electrons one at a time in a sequential process. However, already the monoanion decay chain of Au\textsuperscript{35} in figure 4(a) indicates that a sequential electron emission is not very probable. If there were a significant number of Au\textsuperscript{1−}n clusters that would emit an electron and thus be lost from the trap, the decay chains of sequential neutral monomer evaporation, Au\textsuperscript{1−}n → Au\textsuperscript{1−}n−1 + Au, would be efficiently quenched. Instead, after one electron has been emitted any remaining activation energy seems to lead to neutral monomer evaporation.

To collect further information on the behavior of monoanions and, in particular, of Au\textsuperscript{1−}30 for a direct comparison with Au\textsuperscript{2−}30, the decay studies have been extended by laser activation of the size-selected monoanions, i.e. without the electron bath and electron attachment in the experimental event sequence shown in figure 2. In analogy to figure 7(a), figure 7(c) shows a ToF spectrum before (top) and after (bottom) photoactivation of the precursor cluster monoanion Au\textsuperscript{1−}30. For the particular laser-pulse energy used in this example (22 mJ), only about 30% of the precursors survive. However, essentially all others reappear as monoanions, i.e. the integrated sum of all monoanions of the decay chain adds up to the missing precursor monoanions. The Au\textsuperscript{1−}30 decay behavior has been studied in analogy to the results shown for Au\textsuperscript{2−}30 in figure 7(b). The result of the systematic variation of the laser-pulse energy is shown in figure 7(d). It does not show any significant loss of ions. Even for large pulse energies where about 80% of the precursor monoanion abundance disappears, the same amount reappears in the decay chain as singly charged product clusters. The gray-shaded band shows the integrated relative abundance of all observed anions in the ToF spectrum (1σ-uncertainty band), which fluctuates around 100%. As the anions are not lost, they do not emit their surplus electron. Therefore, it can be concluded that if singly charged clusters are formed from dianions by the emission of one electron, these clusters will further decay by the evaporation of atoms and not electrons. Thus, the emission of two electrons from Au\textsuperscript{2−}30 has to happen simultaneously.

In figure 8(a) the ratio of singly charged product ions to missing ions, i.e. the pathway ratio of one-electron emission in the first reaction process to simultaneous two-electron emission, is plotted as a function of laser-pulse energy (again for the example of Au\textsuperscript{30}). There is no dependence on the laser-pulse energy visible. The data seem to be distributed randomly around the weighted mean of about 35%. Figure 8(b) shows the same ratio, now as a function of cluster size. The data are from the same measurements as shown in figure 5, i.e. the laser-pulse energy was varied between 4 and 7 mJ. The variation of the laser-pulse energy gives a somewhat large fluctuation of the ratio. However, the mean values shown by the gray-shaded area (giving the 1σ-uncertainty band) fluctuates between 20 and 50%. Thus the number of neutralized clusters is at least twice as high as that of singly charged products.

4.3. Pulsed photoexcitation of copper and silver cluster dianions

The measurements have been extended to clusters of the other group-11 elements (coinage metals), i.e. copper and silver. The appearance size of dianionic copper clusters is significantly higher than for gold \cite{12}. Related to this property, the electron affinity is lower as compared with gold clusters of the same size range (see figure 1) and thus electrons are more easily detached than neutral atoms even for relatively large clusters. Thus the experiments have been performed with Cu\textsuperscript{2−}n, \(n = 60, 70, 80\). As an example, the results for Cu\textsuperscript{60} are summarized in figure 9. The
Figure 8. (a) The ratio of singly charged clusters and neutral clusters for Au$_{30}$ as a function of the laser-pulse energy. The dashed line is the weighted average to the data points. (b) The ratio of the number of observed singly charged cluster anions and the number of lost anions (neutral clusters) as deduced from the reference cycle. The gray-shaded band shows the mean value and uncertainty.

case of silver clusters is similar and as a further example the corresponding plots for Ag$_{40}$ are shown in figure 10.

Concerning the photoexcitation of dianions, figures 9(a) and 10(a) show, in analogy to figure 7(b), the exponential decrease of the dianionic precursors as a function of laser-pulse energy and the corresponding appearance of monoanionic cluster products. The integrated relative abundance of all observed cluster anions is shown as a gray-shaded 1σ-uncertainty band. From the latter the fraction of ‘lost ions’ can be deduced, i.e. those clusters which were neutralized after photoexcitation due to two-electron emission. As in the case of gold, most of the products are neutral; for example, for Cu$_{60}$, less than 20% are observed at high laser pulse energies. In the case of silver, there is a significant difference in the behavior as compared to gold and copper: even at pulse energies far below those used in the other cases, the total silver-cluster abundance was reduced to practically zero. In addition, the monoanion abundance does not show a saturation behavior but in contrast, it itself is reduced, too, after an initial increase from zero for low pulse energies.

These results can be compared to those obtained after photoexcitation of the monoanionic clusters Cu$_{60}^{1-}$ and Ag$_{40}^{1-}$ as shown in figures 9(b) and 10(b), respectively. In the case of photoexcitation of Cu$_{60}^{1-}$, about 50% of the monoanionic clusters are lost, i.e. electron emission occurs as a competing process to monomer evaporation in contrast to the behavior of the gold clusters Au$_{30}^{1-}$. However, this ion loss is not as prominent as in the case of Ag$_{40}^{1-}$ where most of the ions are lost due to neutralization after photoexcitation. Electron emission has been observed in other photoexcitation studies on silver cluster anions [44]. Therefore, sequential electron emission from dianionic silver and copper clusters cannot be excluded. Actually, in the case of silver clusters, in the mass range studied in this work, it seems to be a major decay pathway.

Finally, the ratio of singly charged product ions to missing ions has been plotted as a function of laser-pulse energy in figures 9(c) and 10(c). In the case of Cu$_{60}$ this ratio lies at about 20%. Similar to the case of gold, there is no clear tendency towards smaller values at
higher laser-pulse energies. Again, as for the gold clusters, most of the dianions disappear after photoexcitation and only a fraction reappears as monoanions in the ToF spectrum. In the case of Ag$_{40}$ the reduction of the ratio at high laser-pulse energies is more prominent. This is explained by the additional loss of singly charged products after further electron emission.

4.4. Continuous laser irradiation of metal-cluster dianions

In a further series of measurements, a continuous laser irradiation was applied to the stored metal-cluster dianions. The Nd:YAG laser module (Intelite, model GM32-IES) was set to the second harmonic of the ground wavelength, i.e. $\lambda = 532$ nm ($E_{\text{ph}} = 2.33$ eV). As an example, figure 11 shows the result for the case of Ag$_{40}^{2-}$. Instead of the laser-pulse energy, now the
duration of the irradiation was varied. Figure 11(a) shows the exponential decrease of the abundance of the precursor silver-cluster dianions as well as the appearance of the singly charged product clusters. As in the case of pulsed photoexcitation the sum of all observed ions indicates neutralization. Note that the laser profile has a width of $d_L = 3.7$ mm, which is comparable to the width of the cluster distribution (about 1–2 mm). The laser power of $P = 2.9$ mW is very small such that the flux for the given area of the laser profile of about 11 mm$^2$ only gives $\Phi = 8 \times 10^{15}$ s$^{-1}$, i.e. for absorption cross-sections of about 1 Å$^2$ an absorption rate of about seven photons per second is expected. Thus, the absorption of two photons on short time scales is highly suppressed.

The abundance ratio of singly charged to neutral product clusters is constant as in the case of pulsed photoexcitation of gold cluster dianions. This is in sharp contrast to the behavior of silver cluster dianions after pulsed photoexcitation with 3.49 eV photons. Furthermore, the
Figure 11. (a) Relative abundance of $\text{Ag}_{40}^{2-}$ and products $\text{Ag}_{n}^{1-}$ as a function of the duration of irradiation. The gray-shaded area shows the sum of the two relative abundances. (b) Relative abundance of $\text{Ag}_{40}^{1-}$ and products $\text{Ag}_{n}^{1-}, n < 40$, as a function of the irradiation duration. The gray-shaded area shows the sum of the two relative abundances. (c) Ratio of relative abundances of $\text{Ag}_{n}^{1-}$ and neutral product clusters (not observed) as a function of the irradiation duration.

silver-cluster monoanions $\text{Ag}_{40}^{1-}$ only show monomer evaporation under the same experimental conditions (see figure 11(b)) and only a very small amount of electron emission (< 10%) for longer irradiations. Again, this is in clear contrast to the results obtained for $\text{Ag}_{40}^{1-}$ after pulsed photoexcitation with 3.49 eV photons. Therefore, the ion loss due to sequential electron emission can be excluded as in the case of $\text{Au}_{30}^{2-}$ for pulsed photoexcitation and most probably the simultaneous emission of two electrons is the favored decay channel.

5. Coulomb barrier for two-electron emission

The experimental results indicate that under certain circumstances two electrons are emitted simultaneously. Correlated electron emission is known for, e.g., noble gas atoms exposed to
strong laser fields [45–47]. Double photoionization has also been observed in the case of neutral fullerenes [48], which was described by a model using single electron–photon and several electron–electron incoherent collisions [49].

In contrast to these investigations, the dianionic clusters, i.e. systems with two surplus charges, have a Coulomb barrier. In the absence of any further details of the process, the simplest case for simultaneous two-electron emission will be considered, namely the symmetric emission of the two electrons in opposite directions from the cluster as sketched schematically in figure 12(a). The calculation is performed in the framework of the image-charge method, which has been applied successfully for the description of one-electron emission [13]. The two emitted electrons are located at the same distance \( r \) from the center of the sphere in opposite directions. Each electron produces an image charge \( q = eR/r \) at a distance \( r' = R^2/r \) from the center (in the direction of the respective electron), where the cluster radius \( R = R(n) = R_a n^{1/3} \) is the radius of the neutral conducting sphere. The charge \(-2q = -2eR/r\) in the center of the sphere compensates for the image charges, since the sphere itself remains neutral after the emission of the electrons.

The sum of the forces acting on each electron is given by

\[
F(r, R) = \frac{1}{4\pi \varepsilon_0} \left\{ \frac{(-e)(-e)}{(2r)^2} + \frac{q(-e)}{(r-r')^2} + \frac{q(-e)}{(r+r')^2} + \frac{(-2q)(-e)}{r^2} \right\},
\]

where the first term describes the interaction with the other emitted electron, the next two terms are due to the interaction of the electron with the two image charges and the last term describes the interaction with the central charge. As this is the force on each electron and both are moving simultaneously, the integration of \( 2F(r, R) \) leads to a potential

\[
V_{2e}(r, R) = \frac{e^2}{4\pi \varepsilon_0} \left( \frac{1}{2r} - \frac{2R^2}{r^2(r^2 - R^4)} \right).
\]

**Figure 12.** (a) Schematic drawing of a symmetric configuration of two electrons and a neutral conducting sphere for the consideration of two-electron emission of a dianionic metal cluster. For details see text. (b) The Coulomb potential as a function of distance for two electrons (as shown in (a)), which are symmetrically located with respect to a neutral cluster \( \text{Au}_{30}^- \) (solid line), and for a single electron and a singly charged cluster \( \text{Au}_{30}^1^- \) (dashed curve).
for the simultaneous removal of both electrons, with a maximum value determined numerically as

\[ V_{2e,\text{max}}(R) \approx 0.435 \frac{e^2}{8\pi \varepsilon_0} \frac{1}{R} = 0.435 \times V_{1e,\text{max}}(R), \tag{23} \]

i.e. only 44% of the barrier height in the case of single-electron emission [7, 12]. For comparison, the Coulomb barriers for single-electron emission (dashed line) and two-electron emission (solid line) are shown for the case of Au\(^{2-}\) in figure 12(b). Here the barrier height changes from 1.45 to 0.63 eV.

6. Summary and outlook

Size-selected metal-cluster dianions of the elements gold, silver, and copper have been photoexcited in a Penning trap. The resulting mass spectra showed both doubly as well as singly charged product clusters indicating neutral atom evaporation and electron emission (also followed by neutral atom evaporation in the case of sequential decays for sufficient excitation energies). In accordance with the LDM and conducting-sphere approximation which predicts rather high fission barriers, there is no indication of any fission products. Furthermore, the experimental findings confirm the expectations that larger dianionic clusters prefer to evaporate atoms, whereas the smaller ones emit electrons. The ratio of decay rates for monomer evaporation and electron emission as deduced from detailed balance gives a similar trend, although the absolute values of the decay rates do not match the product abundancies observed for the experimental decay period.

In addition, it was found that the cluster-ion signal is missing after photoexcitation. These ‘lost’ ions indicate a neutralization of the doubly charged clusters, i.e. the emission of both excess electrons. Sequential electron emission is ruled out (at least in the case of gold) as the excitation of a singly charged cluster does not lead to electron emission. Instead, neutral monomer evaporation is observed. Thus, the two electrons have to be emitted simultaneously. A possible explanation has been discussed in more detail, namely the simultaneous symmetric emission of the two electrons. Indeed, the Coulomb barrier for such an emission of two electrons is significantly lower than the barrier for the emission of just one electron.

It would be desirable to extend the investigation and observe the clusters after two-electron emission. This will be rather difficult in the case of dianions as neutral products are immediately lost from the trap and are not accessible by mass spectrometry. However, clusters of higher negative charge states have been observed recently for several elements [12, 50, 51] (for an overview, see [26]). Two-electron emission of such a cluster would result in products that are still charged, thus remain stored in the trap and can be detected. If sufficient clusters of higher charge states are produced to allow the present photoexcitation experiments, there would be a chance to shed further light on the decay processes involved.

Another way to investigate the decay behavior with respect to electron emission is through the application of photoelectron spectroscopy. Fullerene dianions have been studied with this technique [52, 53] and the values for the second electron affinity as well as information on the Coulomb barrier were deduced. Thus an extension of the experiment by the attachment of a photoelectron spectrometer to the ClusterTrap setup would be desirable. However, it has to be sufficiently screened from the stray field of the superconducting magnet. Such a setup would allow, firstly, the production of a large number of dianions or clusters with even higher negative
charge states and, secondly, the measurement of photoelectron spectra after ejection of the bunch of size and charge-state selected cluster multi-anions.

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