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Electronic effects in the production of small dianionic gold clusters by electron attachment on to stored Au_n^-, $n = 12-28$

L. SCHWEIKHARD†, A. HERLERT, S. KRÜCKEBERG‡, M. VOGEL

Institut für Physik, Johannes Gutenberg-Universität, D-55099 Mainz, Germany

and C. WALTHER

Institut für Kernchemie, Johannes Gutenberg-Universität, D-55099 Mainz, Germany

ABSTRACT

Single charged gold clusters Au_n^-, $12 \leqslant n \leqslant 28$, are stored in a Penning trap, size selected and transformed into dianions, Au_n^{2-} by the application of an electron beam. At the onset of dianion production, that is that range of cluster sizes n where the smallest doubly charged clusters are observed, the measured intensity ratio of the dianions to their precursors is not a continuous function of cluster size. Instead, there is a strong odd–even effect and a comparatively intense signal of Au_{18}^{2-}. The observed structures are very reminiscent of similar phenomena in the abundance spectra of metal clusters as observed by Knight *et al.* (1984, *Phys. Rev. Lett.*, **52**, 2141), which gave rise to the electronic shell structure interpretation and the further development of the jellium model as applied to metal clusters.

§ 1. INTRODUCTION

In the early 1980s Knight *et al.* (1984) investigated the intensity of neutral sodium clusters as a function of cluster size n as produced in a supersonic expansion with argon carrier gas. Their discovery of structures in the abundance spectra and the interpretation in terms of the domination of the clusters' stability by electronic shell effects was a decisive step in the development of metal cluster research. Soon afterwards Katakuse *et al.* (1985, 1986) found similar abundance effects for singly charged noble metal cluster cations and anions. The shift in the magic numbers, that is the cluster sizes of pronounced signal intensity, as a function of the clusters' charge stage z ($z = -1, 0, 1$) gave further experimental evidence that the stability and thus the structure of monovalent metal clusters is governed by the number of atomic valence electrons: $n_e = n - z$. To first order they can be regarded as a finite-number ensemble of fermions bound to a defined volume by the Coulomb attraction of the atomic cores, much like nucleons confined to atomic nuclei by the strong force (Bjørnholm *et al.* 1991).

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† Author for correspondence.

‡ Present address: The Rowland Institute for Science. 100 E.H. Land Boulevard, Cambridge, Massachusetts 02142, USA.

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The experiments have been extended by several research groups to different metals and further cluster properties, for example dissociation energies, ionization potentials or electron affinities. The extension of the investigations to multiply charged metal cluster cations (Näher *et al.* 1997) and the comparison of clusters of different charge states led not only to additional direct experimental evidence of the significance of the number of atomic valence electrons but also to further parallels in the physics of metal clusters and of atomic nuclei (Bjørnholm 1996). Walter Knight and his group played a leading role in the continued refinement of the experimental techniques and theoretical modelling and interpretation. Examples are the measurements of the cluster's optical response (de Heer *et al.* 1987), photoabsorption spectra (Selby *et al.* 1991), electron attachment experiments (Scheidemann *et al.* 1994), and the further development of the shell including shape deformations, i.e. extension of the spherical to the spheroidal geometry (Clemenger 1985) which describes some of the fine structures in the cluster properties as a function of cluster size. The interested reader will find many more aspects in comprehensive review articles (de Heer 1993, Brack 1993) and recent conference proceedings (*Proceedings of the International Symposium on Small Particles and Inorganic Clusters* 1991, 1993, 1996, 1997, 1999).

Penning-type ion traps have played an important role in the study of metal clusters, mostly with respect to their chemical properties (for example Elkind *et al.* 1988, Irion 1992, Berg *et al.* 1995, Dietrich *et al.* 1996). In addition, the Mainz Cluster Trap (Schweikhard *et al.* 1995, 1999) has been successful in the production (Schweikhard *et al.* 1996, Krückeberg *et al.* 1997a) and study of multiply charged metal cluster cations (Krückeberg *et al.* 1997b, 1999a, Schweikhard *et al.* 1997b, Ziegler *et al.* 1998). Recently, the number of charge states has been complemented by the first observation of dianionic metal clusters (Herlert *et al.* 1999a). In general, free dianionic systems are rare species, in particular the small systems (Scheller *et al.* 1995). In the following we report studies of the abundance pattern of dianionic gold clusters at the appearance size, that is in the size range $12 \leqslant n \leqslant 28$.

§ 2. Experimental set-up and procedure

The apparatus includes an ion source for the production of singly charged metal clusters, a transfer line that delivers them to a Penning trap and a time-of-flight section for the mass analysis of the final ion product distribution. Details of the experimental set-up and overviews of the range of experiments have been given on several occasions (Becker *et al.* 1995, Schweikhard *et al.* 1995, 1999).

The clusters are created by laser vaporization of a metal wire during the application of a helium gas pulse (Weidele *et al.* 1991). The gas–cluster mixture expands adiabatically through a nozzle into the transfer section. Differential pumping stages including two skimmers reduce the helium gas load further away from the source. The cluster ions are guided by electrostatic elements into the field of a 5 T superconducting magnet. They are captured in flight (Schnatz *et al.* 1986) and stored in a Penning trap, a superposition of a homogeneous magnetic field for radial and a quadrupolar electical field for axial ion confinement (with a well depth of 6 V for the present experiments). In such a configuration the ions perform a combination of three independent modes of motion: the harmonic axial trapping motion parallel to and two circular modes perpendicular to the magnetic field direction, the cyclotron and the magnetron motion (Brown and Gabrielse 1986). While the axial mode is due to the electric field and the cyclotron mode due to the magnetic field, the slow drift or

magnetron motion around the trap axis has its origin in the crossed electric and magnetic fields.

The particular trap design (Schweikhard *et al.* 1990) in use at the Mainz Cluster Trap has a hyperbolic geometry with the ring electrode segmented for multiple manipulations of the ion motion. These include the radial ejection of unwanted ions by excitation of the respective cyclotron motion and the centring of the ions of interest in the middle of the trap by the simultaneous application of an argon buffer gas and the conversion of the magnetron into the cyclotron motion by resonant quadrupolar excitation (Bollen *et al.* 1990, Savard *et al.* 1991).

This centring–cooling scheme is essential for the irradiation of the stored clusters with laser or electron beams. It has a further application in the accumulation of several cluster ion pulses where the axial ion motion is damped by the buffer gas and the increase in the magnetron motion due to the damping has to be counteracted (Hasse *et al.* 1994).

For detection and mass analysis the ions are axially ejected from the trap into a time-of-flight (TOF) section. After the 1.5 m drift section, single ion counting is performed by use of a conversion electrode–microchannel plate detector. This configuration allows line-of-sight access into the trap volume as for example for laser experiments (Walther *et al.* 1996a, b, c, Weidele *et al.* 1996, Lindinger *et al.* 1997 Schweikhard *et al.* 1997a, Hild *et al.* 1998). Similarily, electrons emitted from heated rhenium filaments are guided by the magnetic field axially into the trap volume, for example when cluster–electron collisions are to be studied (Herlert *et al.* 1999b, Krückeberg *et al.* 1999b). Owing to the guidance of the magnetic field lines the electron gun can be located off axis between the cluster source and the Penning trap.

Most investigations performed at Mainz have concentrated on the study of positively charged clusters. With the appropriate choice of polarity of the applied electric field, however, anions may be trapped and investigated as well (Weidele *et al.* 1996, 1999a, b). Thus the application of the electron gun that had previously been introduced for the production and study of higher positive charge stages (Schweikhard *et al.* 1996) has recently led to the first observation of dianionic metal clusters (Herlert *et al.* 1999a).

The present investigations are a continuation of these studies. Figure 1 demonstrates the experimental procedure for the case of Au_{25}^{-}. The experimental sequence has been shortened in such ways that each of the four TOF spectra shown represents the status of the sequence after a given event. For the top spectrum (figure 1 (*a*)) a pulse of cluster ions is captured in the Penning trap. The range of cluster sizes is determined by the source, transfer and trap parameters. 90 pulses are accumulated before they are followed by the next event (selection; see below). During the accumulation, one cluster size only is preferentially stored (owing to the application of a fixed-frequency quadrupolar excitation; see above). Nevertheless, some clusters of neighbouring sizes are still present (figure 1 (*b*)). In order to have a defined initial ensemble, the latter are ejected from the trap. Thus a single cluster species, here Au_{25}^{-}, is selected (figure 1 (*c*)). Finally, the electron beam is turned on for a second by switching the filament potential from + 5 V to about − 190 V, that is about − 70 V with respect to the trap. The previous experiments had shown (Herlert *et al.* 1999a) that the application of argon gas pulses during the period of electron irradiation leads to a considerable increase in the yield of dianions. Presumably, the secondary electrons produced by the electron beam stay stored inside the trap and can be picked up by the clusters. Thus, for the present studies, we have made use of this

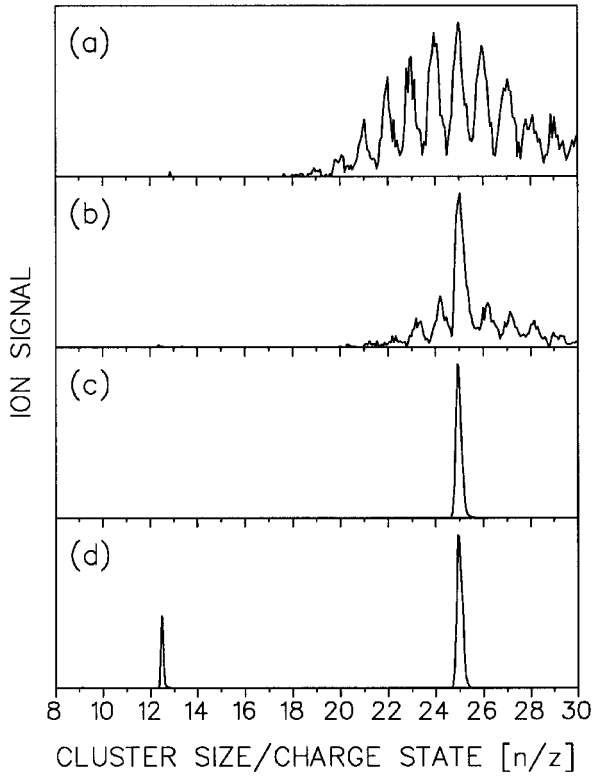

Figure 1. TOF spectra demonstrating the experimental sequence, showing the cluster size distribution (*a*) after capture, (*b*) after the accumulation of 90 ion pulses, (*c*) after selection of Au_{25} and (*d*) after application of the electron beam.

option and several argon pulses have been applied. After a delay of another second a mass spectrum of the resulting cluster ensemble is recorded. Figure 1 (*d*) shows the cluster abundance spectrum after the full sequence with signals at both $n/z = 25$ and 12.5. The latter signal indicates the production of dianionic clusters, Au_{25}^{2-}.

Typical precursor intensities are of the order of about ten counts per sequence. In order to find small amounts of dianions the sequence has been repeated typically a hundred times. In addition to the full sequences, reference sequences have been performed without the application of the electron beam. The reference sequences were interleaved between the full sequences. Thus the cluster production of the source can be monitored quasisimultaneously. While some intensity fluctuations of the cluster source have been encountered, they did not show any systematic trend on the present results. Furthermore, the cluster size of interest has been selected randomly to avoid any bias due to potential drifts of relevant experimental parameters.

§ 3. Results

Before the new results are presented, we summarize the previous findings. Under the experimental conditions of the discovery (Herlert *et al.* 1999a), Au_n^{2-} had been observed for $n = 20$ and above. This appearance size is in fair agreement with approximations of the electron affinity based on the metal-sphere model (see below). The yield of dianions increased continuously between $n = 20$ and $n = 24$

to stay roughly constant for larger clusters. The earlier measurements had been carried out without gas pulses during the electron-beam duration. Typical intensity ratios $I(Au_n^{2-})/I(Au_n^-)$ of dianions to precursor clusters well above the appearance size were of the order of 5%. In contrast, all present experiments have made use of gas pulses for increased dianion yield. In addition, the electron-gun filament has been run on a higher heating current, that is the electron beam intensity has been increased. As in the case of Au_{25}^{2-} (figure 1), and as in the earlier investigations (Herlert *et al.* 1999a), no signs of dissociation reactions have been observed for the singly charged precursor clusters nor for the dianionic products.

Figure 2 shows the relative signal intensity of Au_n^{2-} as a function of cluster size. The cluster size range of the present measurements ($n = 12$ to $n = 28$) has been centred at the previously observed dianion appearance size. Because of the increase in the production efficiency the appearance size has now shifted to lower values. In fact, dianions seem to be produced down to the smallest clusters presently examined ($n = 12$). Note that, in figure 2, several values are given for the dianionic signal intensity of most cluster sizes. These are due to different measurements, that is the data were taken on various days with different parameters such as those of the source, the cluster transfer voltages and the filament heating of the electron gun. Thus, the error bars represent the statistical uncertainties, and the variation in the values indicates the reproducibility of the experimental conditions.

While there is no question as to the existence of most dianionic clusters and in particular the large systems, the small clusters require some further discussion (see also the inset of figure 2 with a magnification of the ordinate scale for the sizes $n = 12$-19). For Au_{12}^{2-} there were 12 counts where an average of 4.7 noise events was expected (as determined for an extended region in the TOF spectrum in the

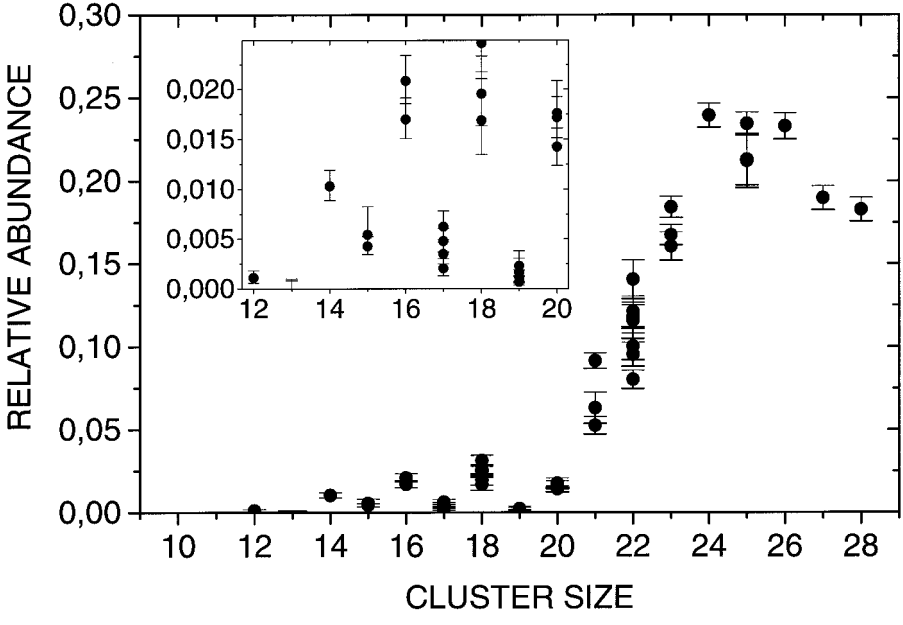

Figure 2. The ratio $I(Au_n^{2-})/[I(Au_n^-) + I(Au_n^{2-})]$ of the number of observed dianions Au_n^{2-} and their respective precursors as a function of cluster size. The insert shows a magnification of the ordinate scale for the cluster size region $n = 12$-19.

vicinity of the expected cluster signal). Thus, under the assumption of a Poisson distribution, the lower and upper limits are 3.9 and 12 respectively (Brandt 1998). (For consistency in the comparison with the dianions of higher abundance a 1σ confidential-limit basis was used throughout the evaluation of the present data.) With 6568 counts of the precursor Au_{12}^{-}, the relative abundance limits are therefore $I(Au_{12}^{2-})/[I(Au_{12}^{-}) + I(Au_{12}^{2-})] = 5.1 \times 10^{-4}$ and 7.2×10^{-4} respectively. In the case of Au_{13}^{2-}, only four counts have been found at a noise level of 6.3 and, when the measurement was repeated one count in an average noise of 1.4. Thus, only upper limits are deduced (Brandt 1998) as indicated in figure 2. The data for $14 \leqslant n \leqslant 19$ have been treated as described for Au_{12}^{2-}. In each case, several measurements indicate the observation of dianions. For the larger clusters $n \geqslant 20$, the number of events was high enough to assume a Gaussian distribution.

§ 4. Discussion

In figure 2 a couple of structures in the dianion abundance as a function of cluster size are observed. Up to $n \leqslant 20$ the dianionic signal intensity is relatively low (i.e. below 3 per cent), rises sharply to almost 25% at $n = 24$ and stays almost constant above this value. For an increased visibility of the fine structure, figure 3 (*a*) shows the averaged dianionic abundance on a logarithmic scale. There is an odd–even effect in the range of small clusters with the even-size clusters dominating. The signal of Au_{18}^{2-} is particularly strong with respect to its neighbours. While there is a slow increase in intensity from one to the next even-sized small cluster, the Au_{18}^{2-} signal is an exception since it is larger than that of Au_{20}^{2-}. In addition, there is a sharp intensity drop at $n = 19$. A dominating Au_{18}^{2-} signal and low Au_{19}^{2-} intensity are in agreement with the expectations due to an electronic shell structure, since the number of atomic valence electrons, $n_e = n - z = 18 - (-2) = 20$, is a magic number. Likewise the even-size clusters have an even number of atomic valence electrons, $n_e = n - (-2)$, which is expected to increase the stability with respect to their odd-size neighbours (Ekardt and Penzar, 1988, Manninen *et al.* 1994, Grönbeck and Rosen 1996).

To gain some further insight the present abundance measurements are compared with energy arguments and other experimental results. Figure 3 (*b*) shows the electron affinity EA (full curve) as estimated for a charged sphere (Makov and Nitzan 1988):

$$EA = WF - \frac{3}{2}\frac{e^2}{4\pi\varepsilon_0 R}, \tag{1}$$

where $WF = 5.31$ eV denotes the bulk work function (Lide 1990), and $R = r_0 n^{1/3}$ is the cluster radius with the Wigner–Seitz radius $r_0 = 1.59 \times 10^{-10}$ m (Lide 1990).

To the smooth functions of the macroscopic model a microscopic fine structure may be added by use of empirical data of electron affinities of neutral gold clusters (Taylor *et al.* 1992). We follow a procedure analogous to that previously performed for the prediction of dissociation energies of doubly charged silver clusters Ag_n^{2+} on the basis of known values for Ag_n^{+} (Krückeberg *et al.* 1999a, d). The deviations $\Delta EA(Au_n)$ of the observed electron affinity from the metal-sphere model predictions are determined for the neutral clusters. These deviations are then used for the correction of the model prediction for the electron affinities of the charged clusters with the same number of atomic valence electrons: $\Delta EA(Au_{n-1}^{-}) = \Delta EA(Au_n)$. The resulting anionic electron affinity predictions are indicated in figure 3 (*b*).

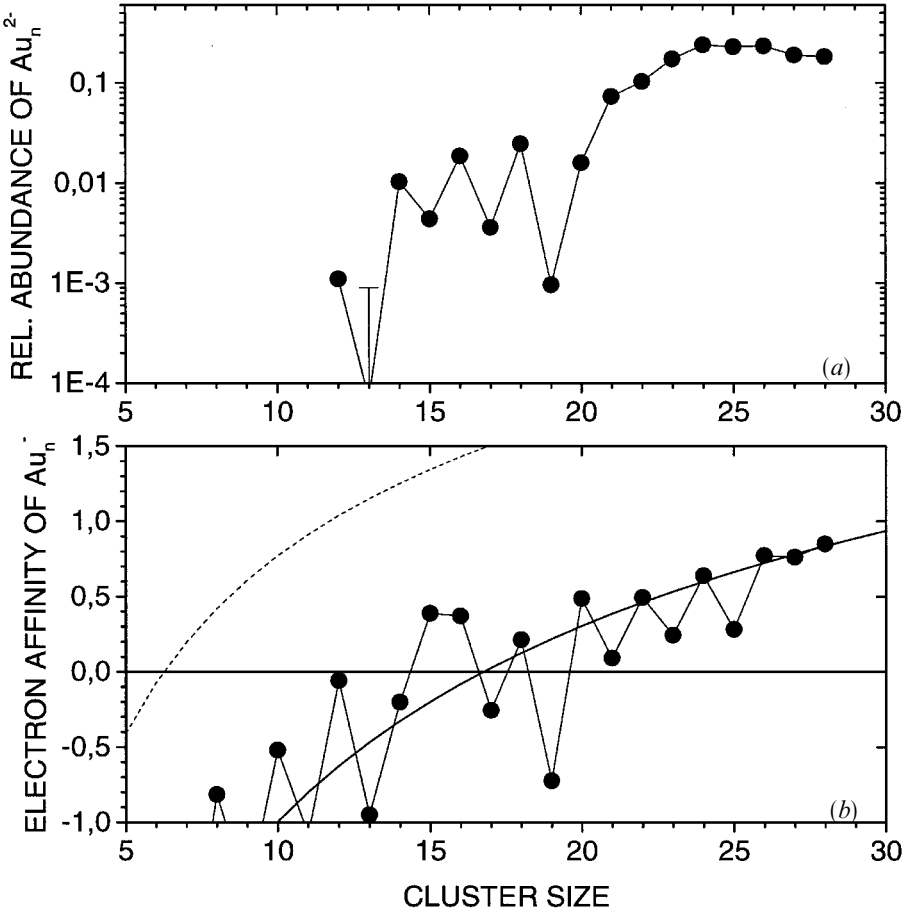

Figure 3. (*a*) The ratio of the number of observed dianions to their respective precursors as a function of cluster size, as in figure 2, but averaged values with a logarithmic ordinate scaling. (*b*) Electron affinities of Au_n^- as a function of cluster size in the metal sphere approximation (equation (1)) (full curve) and with empirical corrections due to experimental values of neutral clusters (Taylor *et al.* 1992) (full circles). The broken curve shows the sum of electron affinities (equation (1)) and Coulomb barrier (equation (2)). (For details see text.)

A comparison of figures 3 (*a*) and (*b*) shows that the relative abundance of Au_n^{2-} and the electron affinities of Au_n^- as functions of cluster size obviously have very similar behaviours with respect to both the general trends and the fine structure. Exceptions are the expected deviation from the electron affinities' odd–even staggering at $n = 15$, which is not reproduced in the abundance spectrum, and the fact that no staggering is observed above $n = 20$ although there had been earlier indications (Herlert *et al.* 1999a) and although it continues to higher cluster sizes in the electron affinities. On the other hand, $n = 19$ stands out both by the low abundance of Au_{19}^{2-} and by the low electron affinity of Au_{19}^-. Both are due to the filled electronic shell at $n_e = 20$.

The predicted electron affinities seem to be too low (even negative) to explain the observation of the small dianionic gold clusters. However, EA is the difference between the energies of Au_n^{2-} and the separated system $Au_n^- + e^-$ where the two particles are assumed to be very far apart. This does not take into account the

Coulomb barrier which has to be overcome (or tunnelled through) in both electron attachment and detachment. Including image charge (i.e. polarization) effects the Coulomb barrier is given by (Jackson 1988)

$$E_C(r) = \frac{e^2}{4\pi\varepsilon_0 R}\left(\frac{R}{r} + \frac{1}{2}\frac{R^2}{r^2} - \frac{1}{2}\frac{R^2}{r^2 - R^2}\right). \tag{2}$$

Its maximum is found at $r_{max}/R = (5^{1/2} + 1)/2$, that is the inverse of the golden ratio $(5^{1/2} - 1)/2$, and its height $E_C(r_{max}) = \frac{1}{2}e^2/4\pi\varepsilon_0 R$ equals the potential energy of two elementary point charges at a distance of $2R$, that is a value of about two electron-volts for the clusters under study. The broken curve in figure 3(*b*) indicates the sum $EA + E_C(r_{max})$. While EA becomes negative at $n \approx 17$, the Coulomb barrier leads to the prediction of smaller (metastable) gold cluster dianions, even far below the cluster sizes of the present study.

However, in order to interpret further the experimental data, tunnelling effects will also have to be taken into account. In analogy to for example simple models of the nuclear α decay, the 'lifetime' of the small dianionic clusters is estimated by the product of a knocking frequency and a tunnelling probability (with a Gamow factor in the exponent)

$$\tau = \frac{2R}{v}\exp\left(\frac{2(2m)^{1/2}}{\hbar}\int_R^{\infty}[E_C(r) - EA]^{1/2}\,dr\right), \tag{3}$$

where m and v are the mass and velocity respectively of the electron. This approximation leads to lifetime predictions larger than the typical experimental event periods of a second only for clusters of size $n \approx 12$ and larger. A more quantitative comparison is outside the scope of this paper. It will have to take into account the conditions and mechanisms of dianion production, the stability of the clusters as well as their internal energy and its distribution with respect to the various degrees of freedom.

§ 5. Conclusions and outlook

In this first study on the properties of dianionic metal clusters we have measured the relative abundances as a result of electron attachment to monoanionic systems while stored in a Penning trap. Odd–even and shell closure features have been observed for clusters which are in line with the expectation from electronic structure considerations and which are similar to the early abundance measurements on neutral alkali and singly charged noble-metal clusters. While the details of the production mechanism are not yet known it is possible to convert a substantial number of singly charged stored clusters into dianionic species, if the clusters are sufficiently large ($n \geqslant 20$). Thus a whole new field of cluster research has been opened, where all established techniques to probe the clusters' properties can be applied (Schweikhard *et al.* 1999). Note that excited dianionic clusters have a large number of different decay pathways to choose from: evaporation of neutral atoms or larger fragments, fission into two charged fragments and emission of an electron, in addition to radiative cooling. Both collision (Becker *et al.* 1994, Ziegler *et al.* 1998, Krückeberg *et al.* 1999c) and time-resolved photodecay experiments (Walther *et al.* 1996b,c, Lindinger *et al.* 1997, Hild *et al.* 1998) should provide information about the pathways and the respective threshold energies. As for chemical reactions, it remains to be seen which reactions actually occur and which are prevented by the dominance of electron transfer processes.

Let us note in passing that other production schemes may be employed as well. Metal cluster dianions have recently been observed in laser desorption experiments under ultrahigh-vacuum conditions (M. M. Kappes 1999, private communication). With respect to theoretical studies, there are so far only a few publications (Yannouleas and Landman 1993a, b). Presumably this is due to the lack of experimental counterparts which the calculated results could be checked against. Since this has now changed, the emerging new field is expected to gain momentum with respect to both experimental and theoretical investigations.

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