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First Observation of Doubly Charged Negative Gold Cluster Ions

A. Herlert,[1] S. Krückeberg,[1] L. Schweikhard,[1] M. Vogel[1] and C. Walther[2]

[1] Institut für Physik, Universität Mainz, D-55099 Mainz, Germany
[2] Institut für Kernchemie, Universität Mainz, D-55099 Mainz, Germany

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Abstract

Singly charged gold cluster anions in the size range $n = 16 - 30$ have been captured, stored and size selected in a Penning trap. After application of an electron beam doubly charged gold cluster anions have been observed for $20 \leq n \leq 30$. To our knowledge this is the first observation of metal cluster dianions. The threshold appearance size is in good agreement with a simple charged sphere model. The application of argon gas pulses simultaneously with the electron beam is found to increase the production rate by an order of magnitude.

1. Introduction

The stability of free dianions has been of continuous interest over the past decades [1]. While the observation of atomic and diatomic dianions in the gas phase is debated, several molecular dianions have been produced. As for atomic and molecular clusters, doubly charged negative carbon clusters from a graphite sputter source [2] have been observed in the size range $n = 7 - 28$, fullerene dianions C_{60}^{2-} were found by laser-vaporization of a C_{60} sample [3] and electron attachment to C_{84}^{-} has been achieved [4]. Recently, alkali halide cluster dianions were produced in an electrospray soure, e.g. $Na_6Cl_8^{2-}$ [5]. However, to the authors' knowledge no pure metal cluster dianions have been observed so far. On the theoretical side, extended calculations have been performed for doubly charged negative sodium clusters only [6].

2. Experimental setup and procedure

Reviews of the Mainz Cluster Trap have been presented recently [7]. The experimental procedure is demonstrated in Fig. 1 by time-of-flight (TOF) spectra of the cluster ensemble in the trap at different stages of the experiment for the case of electron attachment to Au_{24}^{-}. Singly charged metal clusters produced by a laser vaporization source are transferred to, accumulated and centered in a Penning trap (Fig. 1a). One cluster size (Au_{24}^{-}) is selected by radial ejection of all other ions (Fig. 1b). Subsequently, a 70 eV electron beam is directed through the trap for 600 ms. The charged products remain stored in the trap until all ions are axially ejected and analyzed by TOF mass spectrometry (with single ion detection by a conversion dynode detector). In the case of Au_{24}^{-} selection prior to the application of the electron beam an additional signal at $n/z = 12$ is observed which indicates the production of doubly charged negative clusters Au_{24}^{2-} (Fig. 1c).

3. Results and Discussion

Clusters in the size range $n = 16 - 30$ have been investigated. Figure 2 shows the resulting TOF spectra for $n = 18 - 25$, where the left part of the spectra is magnified by a factor of 10. Additional signals appear only at half the n/z value of the size-selected precursor Au_n^{-}. A dissociation of the form $Au_n^{-} \rightarrow Au_{n/2}^{-} + Au_{n/2}$ seems very unlikely, since singly charged both positive and negative gold cluster ions of the present size range are known to decay by neutral monomer evaporation [8]. In addition, the signal at $(n/z)/2$ appears even in the case of odd-size clusters, i.e. at half-integer n/z values. We therefore conclude that dianionic gold clusters have been produced.

The ratio $I(Au_n^{2-})/I(Au_n^{-})$ of the intensities of singly and doubly charged clusters has been plotted in Fig. 3 as a function of cluster size. No doubly charged anions are observed below $n = 20$. The abundance of dianions increases in the range $n = 20 - 24$ and remains roughly constant above $n = 24$. The present appearance size, the threshold size of observation, may depend on the details of the experiment

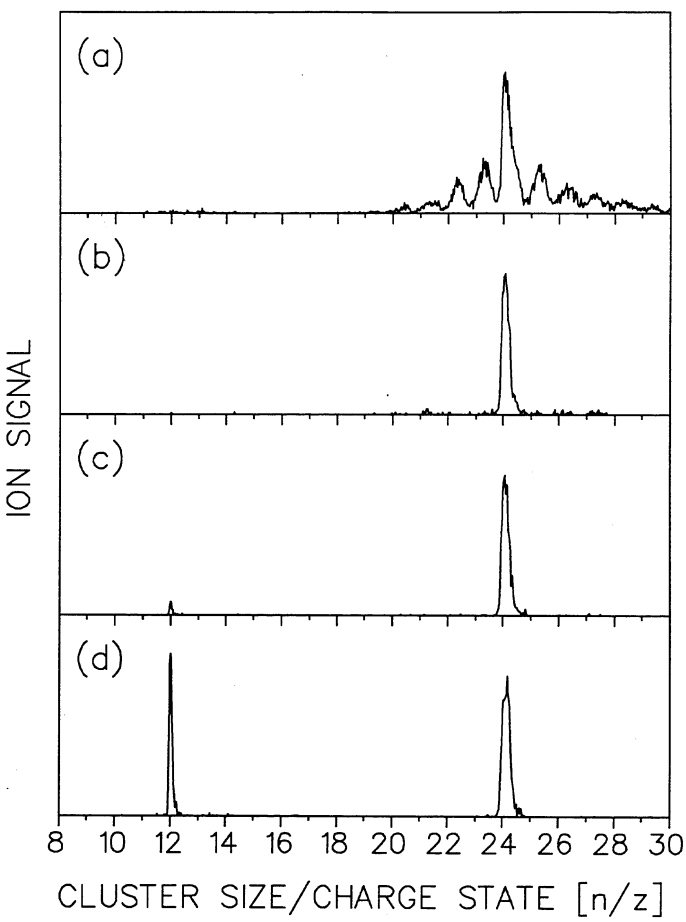

Fig. 1. Experimental sequence for the production of Au_{24}^{2-}. For details see text.

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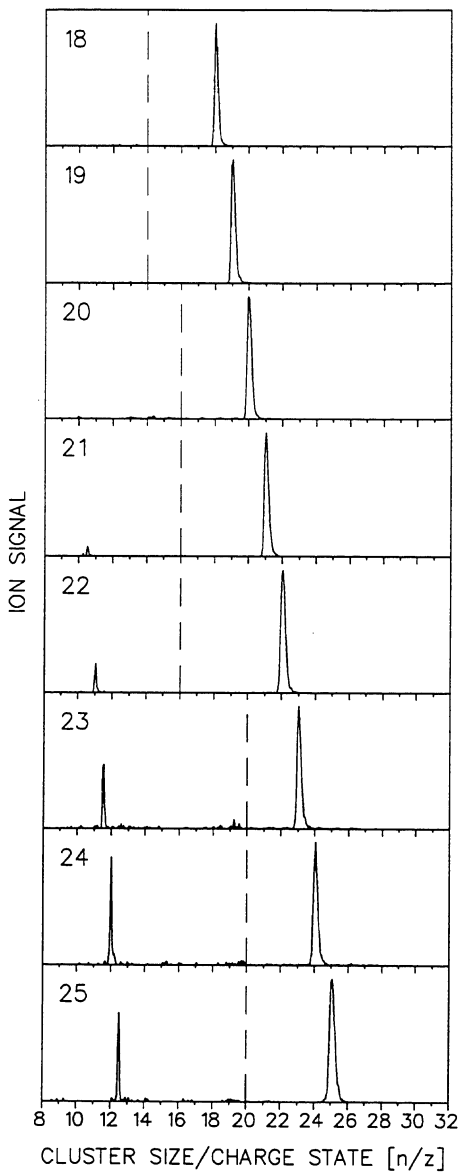

Fig. 2. TOF-spectra after application of the electron beam to size-selected Au_n^-, $n = 18 - 25$. The left part of the spectra is magnified by a factor of 10.

such as the production mechanism and the statistics as well as the stability of the gold cluster dianions.

For comparison, the electron affinity of a gold cluster with charge state $-z$ can be estimated by use of a charged sphere model [9]:

$$EA(n, -z) = W_F - (z + 0.5)\frac{e^2}{4\pi\varepsilon_0 \cdot r_0 \cdot n^{1/3}}. \quad (1)$$

where W_F denotes the bulk work function ($W_F = 5.31$eV [10]) and r_0 the constituent radius at room temperature ($r_0 = 1.65 \cdot 10^{-10}$m [10]). The resulting electron affinities for neutral and singly charged gold clusters, Au_n^0 and Au_n^{1-} respectively, are shown in Fig. 4. Whereas all neutral gold clusters have a positive electron affinity, the singly charged anions below $n = 17$ show a negative electron affinity, i.e. are unstable towards electron emission. The transition size depends on the parameters used for the liquid drop model. If, e.g., the consituent radius at the melting point ($r_0 = 1.59 \cdot 10^{-10}$ m [10]) is taken, the electron affinity of gold cluster anions becomes negative below $n = 15$. It should also be noted, that these macroscopic calculations completely neglect microscopic effects, i.e. shell and odd-even-effects [6]. In addition, the production mechanism may shift the appearance size to larger values. Thus, within the present approximations, a good agreement between the experimental appearance size ($n = 20$) and the theoretical size limit for negative electron affinity ($n = 15 - 17$) is found.

As for the production mechanism, the electrons with an energy of $E \approx 70$ eV will most probably not lead to direct electron attachment, but rather to the removal of the excessive electrons of the stored anions, i.e. to neutralization (possibly further ionization [11]) and loss of the clusters. If however, neutral background atoms or molecules are ionized by electron impact inside the trap, the resulting secondary electrons will stay stored inside the trap and can eventually attach to the simultaneously stored clusters. To check this hypothesis, we have intentionally increased the pressure during the application of the electron beam by pulses of argon gas. The result for Au_{24}^- is shown in

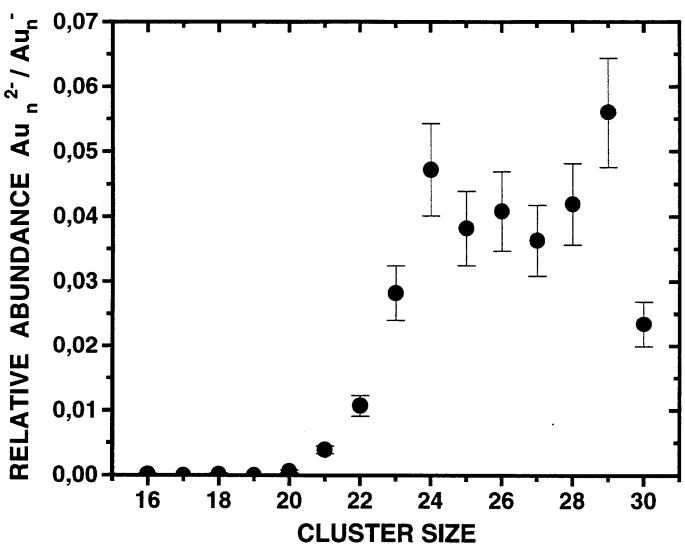

Fig. 3. Ratio of doubly to singly charged gold cluster anions. For details see text.

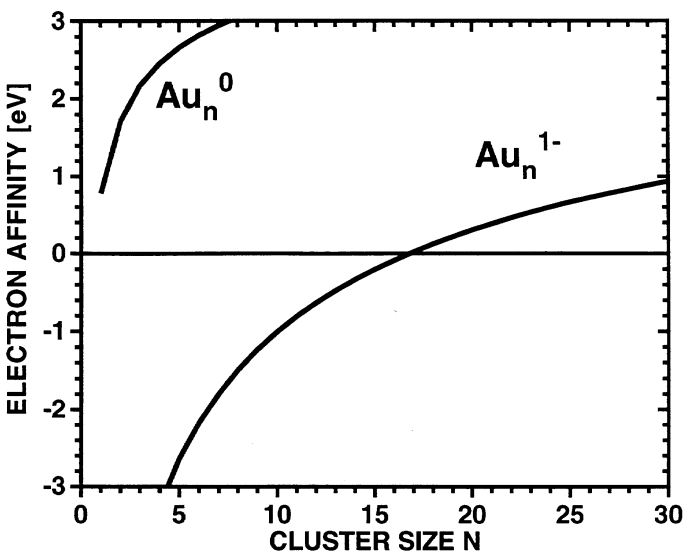

Fig. 4. Electron affinities of gold clusters as given by the charged sphere model Eq. (1).

Fig. 1d: a significant increase of intensity of the $n/z = 12.0$ signal with respect to the intensity in the absence of the argon pulses (Fig. 1c). Appearently the sea of stored secondary electrons helps to produce Au_n^{2-}.

In another experimental sequence the Penning trap has been filled with electrons by electron impact ionization of neutral argon prior to the capture of the singly charged gold clusters. While the signal intensity of the resulting Au_n^{2-} is larger than for the original sequence described in section 2, it was lower than in the case of argon-pulse assisted secondary-electron production during cluster trapping. It may well be that in the case of the creation of the sea of stored electrons prior to the cluster capture, the electrons have cooled down before the clusters arrive and are not as likely to overcome the Coulomb barrier for attachment. The details of the production mechanism will be subject to further investigations. It may already be pointed out, that in contrast to direct electron impact on positively charged metal clusters [11] no dissociation has been observed, neither of the singly nor of the doubly charged cluster anions.

4. Conclusion

Gold cluster dianions have been produced in a Penning trap by the application of an electron beam during the storage of singly charged clusters. The threshold appearance size is in good agreement with the expectations from a charged sphere model. Preliminary measurements indicate that the production of Au_n^{2-} is due to the attachment of secondary electrons formed by electron impact ionization of neutral atoms or molecules inside the trap. The details of the dianion production mechanism are to be investigated. In addition, we plan to extend the investigations to other elements and to probe the properties of the dianionic clusters by the methods that have already been established for singly and multiply-positively charged species [7].

Note added in proof

After completion of this manuscript we have heard from Prof. M. M. Kappes (Univ. of Karlsruhe) that his group has recently observed metal cluster dianioins upon laser irradiation of metal targets under ultra-high-vacuum conditions. A publication is in preparation.

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References

1. Scheller, M. K., Compton, R. N. and Cederbaum, L. S., Science **270**, 1160 (1995).
2. Schauer, S. N., Williams, P. and Compton, R. N., Phys. Rev. Lett. **65**, 625 (1990).
3. Hettich, R. L., Compton, R. N. and Ritchie, R. H., Phys. Rev. Lett. **67,** 1242 (1991); Limbach, P. A., Schweikhard, L., Cowen, K. A., McDermott, M. T., Marshall, A. G. and Coe, J. V., J. Am. Chem. Society **113**, 6795 (1991).
4. Compton, R. N., Tuinman, A. A., Klots, C. E., Pederson, M. R. and Patton, D. C., Phys. Rev. Lett. **78,** 4367 (1997).
5. Friedrich, J., Weis, P., Kaller, J., Whetten, R. L. and Kappes, M. M., submitted to Eur. Phys. J. D.
6. Yannouleas, C. and Landman, U., Phys. Rev. B **48**, 8376 (1993); Chem. Phys. Lett. **210**, 437 (1993).
7. Becker, S. Dasgupta, K., Dietrich, G., Kluge, H.-J., Kuznetzov, S., Lindinger, M., Lützenkirchen, K., Schweikhard, L. and Ziegler, J., Rev. Sci. Instr. **66**, 4902 (1995); Schweikhard, L., Becker, S. T., Dasgupta, K., Dietrich, G., Kluge, H.-J., Kreisle, D., Krückeberg, S., Kuznetsov, S., Lindinger, M., Lützenkirchen, K., Obst, B., Walther, C., Weidele, H. and Ziegler, J., Physica Scripta **T59**, 236 (1995); Schweikhard, L., Krückeberg, S., Lützenkirchen, K. and Walther, C., submitted to Eur. Phys. J. D.
8. Becker, S., Dietrich, G., Hasse, H.-U., Klisch, N., Kluge, H.-J., Kreisle, D., Krückeberg, S., Lindinger, M., Lützenkirchen, K., Schweikhard, L., Weidele, H., Ziegler, J. Z. Phys. D **30,** 341 (1994); Weidele, H., Vogel, M., Herlert, A., Krückeberg, S., Lievens, P., Liverans, R. E., Schweikhard, L. and Walther, C., submitted to Eur. Phys. J. D.
9. Makov, G. and Nitzan, A., Chem. Phys. **88,** 5067 (1988).
10. Lide, D. R. (ed.), "CRC Handbook of Chemistry and Physics", 71st edition (CRC Press, Boca Raton, 1990).
11. Schweikhard, L., Beiersdorfer, P., Bell, W., Dietrich, G., Krückeberg, S., Lützenkirchen, K., Obst, B. and Ziegler, J., Hyp. Int., **99,** 97 (1996); Krückeberg, S., Dietrich, G., Lützenkirchen, K., Schweikhard, L., Walther, C. and Ziegler, J., submitted to Eur. Phys. J. D; Herlert, A., Krückeberg, S., Schweikhard, L., Vogel, M. and Walther, C., submitted to J. Electron Spectrosc. Relat. Phenom.

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