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International Journal of Mass Spectrometry 213 (2002) 157–161

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Photoinduced dissociation of anionic and electron detachment of dianionic gold clusters by use of a laser pointer

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Received 12 July 2001; accepted 16 August 2001

Abstract

Size-selected anionic and dianionic gold clusters have been stored in a Penning trap and irradiated with the green light of a laser pointer. As examples of special interest, the systems Au_7^- and Au_{29}^{2-} have been chosen. In particular, Au_7^-, a small gold cluster with closed electron shell, is observed to decay into Au_6^- and Au_5^- with a decay pathway branching ratio similar to that of Au_9^+. The dianionic cluster Au_{29}^{2-} shows electron detachment upon photoexcitation. This observation is in agreement with independent experiments [Stoermer et al., Int. J. Mass Spectrom. 201 (2001) 63], where Au_{29}^{2-} is found to be the smallest dianion produced by neutral monomer evaporation of hot dianionic gold clusters. (Int J Mass Spectrom 213 (2002) 157–161)

Keywords: Metal clusters; Dianions; Photodissociation; Photodetachment; Penning trap

1. Introduction

When atomic clusters are heated up they can release their excess energy through various competing decay channels such as evaporation of neutral constituents, fission into charged fragments, thermionic emission of electrons or radiative cooling, i.e. emission of blackbody-like radiation (see e.g. [1–3]). During the last few years, several collision-induced-dissociation experiments with transition metal cluster anions have been reported [4–8] which resulted in mostly qualitative knowledge of the systems' decay pathways. In particular, the fragmentation behavior of the anions M_{n-1}^- (where "M" stands for the element of interest and the subscript describes the number of atoms of the cluster) has been found to be similar to that of the cations M_{n+1}^+. This is a strong indication that the corresponding number of atomic valence electrons n is responsible for the systems' properties.

Recently, cationic gold clusters have been investigated by photoexcitation in order to quantitatively study not only their fragmentation pathway branching ratios as a function of cluster size [9], but also to investigate these branching ratios as a function of the excitation energy [10]. In the present experiments, these investigations have been extended to anionic clusters. Instead of applying a pulsed dye laser system as before [11,12], a much simpler device has been

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Dedicated to H.-J. Kluge who has continuously supported the Cluster Trap (up to the supply of his laser pointer for the present work) on the occasion of his 60th birthday.

1387-3806/02/$22.00
PII S1387-3806(01)00529-2

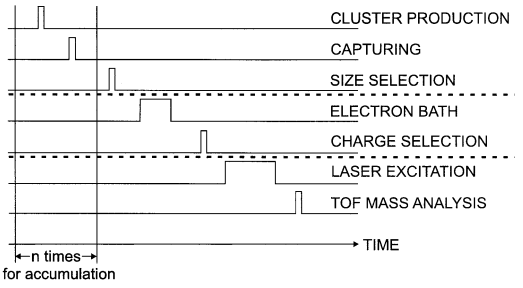

Fig. 1. Experimental sequence. The electron bath and the charge selection are only applied in case of the dianionic clusters (for details see text).

used for photoexcitation. In the following, we present experiments on the activation of stored anionic and dianionic gold clusters with the green light of a laser pointer. This procedure does not allow to follow the processes in a time-resolved manner as in earlier studies of delayed electron emission of tungsten clusters, W_n^- [13,14]. However, the emphasis of the present studies is not on the time structure of the decay, but on the possible competition between the decay pathways, i.e. electron emission and evaporation of neutral atoms and dimers.

Two particularly interesting systems have been chosen for these studies: (1) Au_7^- with a shell closure at eight atomic valence electrons, which can be compared to the isoelectronic system of Au_9^+ [9] and (2) Au_{29}^{2-}, which has been reported to be the smallest dianionic gold cluster produced from hot larger dianionic precursors [15]. Thus, whereas larger clusters are expected to show a significant propensity toward neutral monomer evaporation upon excitation, $Au_n^{2-} \rightarrow Au_{n-1}^{2-} + Au$, the cluster Au_{29}^{2-} should exclusively show electron emission $Au_{29}^{2-} \rightarrow Au_{29}^- + e^-$ [15].

2. Experimental procedure

The experimental setup has been described in detail elsewhere [12,16–18]. In the present case of the cluster anions, the experimental sequence consists of the following steps (see Fig. 1): (1) production of cluster anions in a Smalley-type laser vaporization source [19,20]; (2) transfer to the Penning trap and capture in flight [21]; (3) accumulation of several cluster-ion bunches by multiple application of steps (1) and (2) [22]; (4) size selection by resonant radial ejection of all other species from the trap; (5) irradiation with the beam of a green laser pointer for several seconds; (6) ejection of the ions into a time-of-flight (TOF) mass spectrometer. Typically, a single sequence results in the observation of about 30 ions. The sequence is repeated up to a hundred times and the spectra are added to increase the statistical significance. Alternating with the actual laser-excitation sequence, a reference sequence is performed, where the laser beam is not applied. This allows the data to normalize to a quasisimultaneous reference measurement.

Since the cluster source produces only singly charged (and neutral) clusters [20], the sequence has to be extended for the dianion measurements [23]. In addition to the events described previously, after step (4) the size-selected singly charged cluster anions are subjected to an electron bath in the trap for about 2 s. To this effect a beam of primary electrons is guided axially through the trap while simultaneously argon gas pulses are applied to the trap volume. By the ionization of the argon atoms secondary low-energy electrons are produced which stay trapped like the anions. As reported earlier this leads to the production of dianions [24–26] which are subsequently charge-selected by ejection of the remaining singly charged clusters. By this procedure an ensemble of size- and charge-selected dianionic gold clusters is formed and stored in the trap and the sequence continues with the irradiation of this ensemble [step (5)].

A frequency-doubled diode-pumped Nd:YAG laser pointer (Roithner Lasertechnik model GP-4 with a wavelength of 532.2 nm, corresponding to a photon energy of 2.33 eV) has been employed for photoexcitation. The AAA batteries have been removed and the laser pointer has been operated with an external power supply. The output of the laser pointer has been limited to an average power of 0.34 mW, which is delivered in a quasicontinuous beam (duty cycle of 50% at a pulse repetition rate of 263 Hz). The excitation period was controlled by gating the power supply for a given time (5 or 10 s, see the following). No further optical elements were used, and the laser

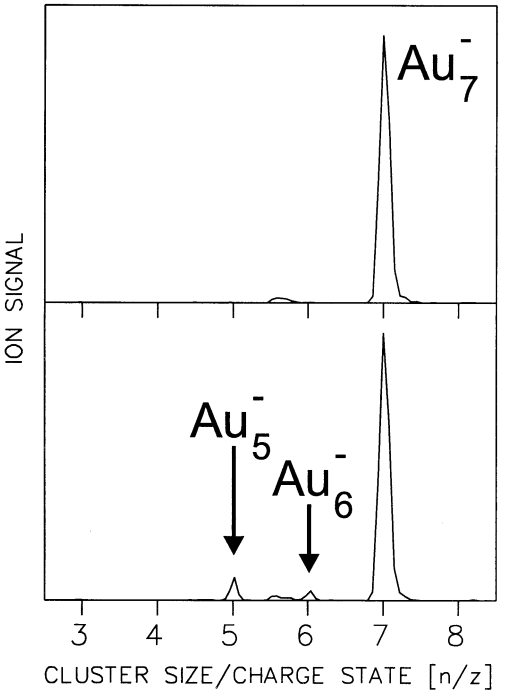

Fig. 2. TOF mass spectra of the gold cluster Au_7^- without (top) and with irradiation (bottom) with a 0.34 mW green laser pointer beam for 5 s.

beam was sent into the vacuum system and axially through the trap by way of a Suprasil window. At the position of the cluster trap (3.5 m from the laser pointer) the beam had a diameter of about 3 mm. Unfortunately, it was not possible to stabilize the laser pointer to a constant output power. Thus, long-term and also short-term fluence variations prevented detailed studies, as, e.g. with respect to the decay yield as a function of the duration of the laser irradiation. Nevertheless, these low-budget experiments give valuable information about the decay pathways of the selected gold clusters.

3. Results and discussion

3.1. Anion Au_7^-

Fig. 2 shows time-of-flight spectra of Au_7^- without (top) and with 5 s irradiation (bottom) with the laser-pointer light. The excitation leads to fragments Au_6^- and Au_5^- with an intensity ratio of $I(Au_5^-)/I(Au_6^-)=2.54(74)$. By comparison with similar experiments on cationic gold clusters [9,10,27] it can be assumed (1) that the decay occurs only upon absorption of at least two photons and (2) that the sequential decay $Au_7^- \rightarrow Au_6^- \rightarrow Au_5^-$ is energetically highly suppressed, i.e. (most of) the Au_5^- products are the direct result of neutral dimer evaporation.

There have been as yet no reports about the fragmentation pathway branching ratios $d/m=I(Au_{n-2}^-)/I(Au_{n-1}^-)$ between neutral dimer and neutral monomer evaporation for the anionic gold clusters, but a comparison with the fragmentation of cations [10] shows that the decay behavior is governed by the system's electronic properties. With eight atomic valence electrons Au_9^+ is the corresponding cation of Au_7^-. The branching ratio d/m for Au_9^+ has a high value at energies in close proximity to the dissociation energy of about 3.3 eV, and decreases with increasing excitation energy, i.e. significant monomer evaporation is observed at high excitation energies. This behavior can be quantified by the empirical expression [10]

$$d/m = \exp\left[s(n)\,E + s_0(n)\right]$$

with $s(9)=-0.98(8)\ \mathrm{eV}^{-1}$ and $s_0(9)=5.5(3)$ for Au_9^+. This formula leads to a branching ratio d/m at 5.0 eV total excitation energy (0.32 eV thermal energy at room temperature plus 4.66 eV laser excitation energy) of $d/m=1.8(9)$. In other words, about 1/3 of the decay are expected to be monomer evaporation, which is in agreement with the present experimental value of $(28\pm8)\%$ for Au_7^-. Possible higher numbers of absorbed photons (three-photon absorption and greater) would shift the expected portion of monomer emission to lower values, thus even reducing the already small difference between measurement and expectation.

As for radiative cooling, it is not expected to occur with a significant rate. Calculations similar to those performed in [28] (with the bulk optical response function for gold [29]) show that the dissociation rate is several orders of magnitude higher. Since the optical response and thus the absorption and emission

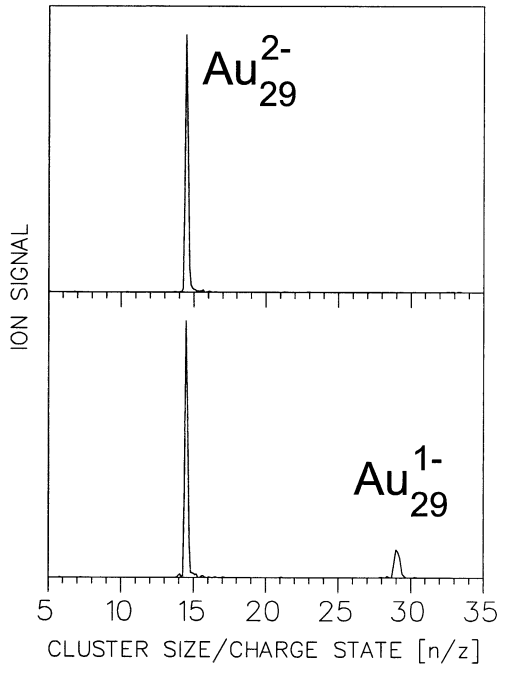

Fig. 3. TOF mass spectra of the gold cluster Au_{29}^{2-} without (top) and with irradiation (bottom) with a 0.34 mW green laser pointer beam for 10 s.

cross section of small anionic and dianionic systems may differ from bulk behavior, radiative cooling of the systems under investigation cannot be completely ruled out. However, radiative cooling is only expected to quench the fragmentation process to some extent, but not to alter the observed branching ratio of the fragmentation processes.

3.2. Dianion Au_{29}^{2-}

Fig. 3 shows the time-of-flight spectra of Au_{29}^{2-} without (top) and with irradiation (bottom) with green laser pointer light for 10 s. Upon photoexcitation, one excess electron is detached, leading to the appearance of the singly charged species Au_{29}^{-} in the mass spectrum. No significant monomer evaporation has been found, only electron detachment for about a 15% fraction (supposedly due to the limited laser fluence and spatial overlap between the cluster ensemble and the laser beam).

This experimental result is in agreement with independent measurements [15], where gold cluster dianions are produced upon pulsed UV laser ablation of metal surfaces under high vacuum conditions. In the resulting mass spectrum, a chain of large gold cluster dianions is found to end at a threshold size of $n=29$, which is interpreted as the vanishing of monomer evaporation as an alternative cooling process to electron emission. Note, that fission into two charged fragments has neither been observed in previous nor in the present investigation of dianionic metal clusters. The present measurements explicitly confirm the mechanism of electron emission from excited Au_{29}^{2-} as the dominant *m/z*-changing cooling mechanism. Thus, smaller dianionic gold clusters cannot be produced by evaporation of neutral atoms from Au_{29}^{2-}. In contrast, systems as small as Au_{12}^{2-} have been observed with a different production procedure, namely the application of an "electron bath" to stored singly charged gold clusters, Au_n^- [24–26].

4. Conclusion

The light of a green laser pointer has been used for the photoexcitation of stored singly and doubly charged anionic gold clusters. In the case of Au_7^- agreement has been found between the observed and the expected fragmentation pathway branching ratios for dimer and monomer decay. This indicates that the details of the fragmentation process are governed by the electronic properties of the systems under investigation. The measurements have been extended to the case of the dianion Au_{29}^{2-}. For this case the dominant cooling mechanism is observed to be the emission of an excess electron. This behavior is in agreement with the interpretation of independent measurements [15].

Acknowledgments

This work has been supported by the DFG, the "Materialwissenschaftliches Forschungszentrum Mainz" the "Fonds der Chemischen Industrie" and the EU networks "Eurotraps" and "Cluster Cooling."

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