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# Intense emission of cluster anions from gold targets under impact of keV/u gold clusters.

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## Abstract

Under impact of 150 keV/atom  $\text{Au}_n^+$  projectiles ( $1 \leq n \leq 9$ ) on gold targets the emission yield of anionic clusters increases much faster with  $n$  than expected from simple proportionality. Moreover the anion size distribution is much wider for bombardment by clusters. The cluster yield enhancements reflect the size dependence of the cluster stability according to the electronic shell structure. Accordingly, the most intense emission is observed for  $\text{Au}_7^-$ : under  $\text{Au}_9^+$  impact the  $\text{Au}_7^-$  yield per incident atom is enhanced by a factor of  $\sim 6$ .

When a heavy atom cluster accelerated in the keV/u energy range penetrates into a solid, the collision cascades initiated by the individual atoms of the cluster overlap, leading to an increase of the density of the deposited energy in comparison to the energy density deposited by an atomic ion of the same velocity. Subsequent phenomena, such as material modifications or surface emissions, are enhanced under the impact of an n-atom cluster with respect to what would be expected from the sum of the effects of n atomic ions. This nonlinear effect has been observed since the seventies in the collisional sputtering of metals by diatomic ions [1]. More recently, the availability of gold cluster beams has led to detailed investigations of these effects, particularly their cluster-size and velocity dependences [2]. Very large sputtering yields, associated with the formation of surface craters, have been observed : for example more than 10000 gold atoms are on the average ejected from a gold target by single cluster impact ( $\text{Au}_{11}^+$  or  $\text{Au}_{13}^+$  of energy  $\sim 100$  keV/atom). With such large numbers of ejected atoms, there is a great need of information on the nature of ejected species (atoms, clusters, chunks?) which are produced in extreme conditions of energy density ( $\sim 100$  keV/nm over areas in the  $\text{nm}^2$  range). If postionization methods can bring relevant data in that respect, they however do not provide an absolute measure of neutral cluster abundance, since the postionized cluster size distributions result from cluster size-dependent ionization potentials and depend on cluster vibrational excitation. As ions are already presents in sputtered matter, the study of this ionized fraction of ejected matter can bring relevant data on cluster-solid interaction, such as those we have obtained from ion mass spectrometry experiments using a Time of Flight (TOF) detection. The experimental results we report in this paper deal with the negative ion emission from gold targets under the impact of  $\text{Au}_n^+$  clusters ( $n = 1-9$ ) accelerated at an energy of 150 keV/atom, an energy for which the anion emission yields have been observed to be maximum [3]. Gold clusters being accelerated as

continuous beams, the start signal needed for TOF experiments is easily obtained in negative ion emission from the concomitant electron emission.

Enhanced secondary ion emission from gold and organic targets [4], from tantalum, niobium and silicon targets [5], has already been observed for incident gold clusters of small size ( $n = 1-5$ ) at low energy (a few keV/atom). In addition, the emission yields from organic (biomolecules) and inorganic (CsI) targets have been found to be maximum at an incident energy of about 50-80 keV/atom [6]. In the case of niobium and tantalum targets, the emission yields per incident atom of the positive monomers have been found to be enhanced by a factor between 2 and 9 under  $Au_2^-$  and  $Au_3^-$  bombardment [5]. In this work, rather huge yields are reported for the emission of larger clusters since  $Nb_9^+$  and  $Ta_{10}^+$  emission yields are enhanced by two orders of magnitude under  $Au_3^-$  impacts. For gold targets, the only available data are for the emission of the negative monomer, that is observed to be enhanced by a factor of  $\sim 2$  under impact of  $Au_2^+$  and  $Au_3^+$  clusters [4].

The gold cluster beams are delivered by the 2.5 MV Van de Graaff accelerator of the Institut de Physique Nucléaire de Lyon, equipped with a liquid metal ion source (LMIS). After acceleration the gold clusters are mass selected by means of an analysing magnet. This facility and the cluster beam line have been described previously [2,7]. For ion emission experiments, the beam intensity is reduced down to about 3000 clusters/s by two collimators, located 1.7 m apart on the beam line, defining a beam spot on the target of about 250  $\mu\text{m}$  in diameter. Prior to each measurement the cluster beam is charge and energy analyzed [7,8] in order to assess the integrity of the clusters at the target site: The fraction of neutrals and fragments produced in collisions along the beam line does not exceed 2% of the total beam in all the measurements.

The target is a high purity (99.99%) gold foil 100- $\mu\text{m}$  thick. The residual pressure in the experiment chamber is in the  $10^{-8}$  mbar range. Prior to ion emission measurements the target surface was sputter-cleaned using high intensity ( $> 100$  pA)  $\text{Au}_n^+$  beam at a fluence of  $10^{15}$  Au ions/ $\text{cm}^2$  in order to remove the air formed impurity layer. This procedure leads to reproducible mass spectra of the emitted ions as observed in successive measurements. The target normal makes an angle of  $30^\circ$  with the beam direction. The electrons and the  $\text{Au}_p^-$  ions emitted from the gold target at each impact are accelerated between the target biased at -6 kV and a grounded electrode facing the target at a distance of 2.6 mm. Then they enter a grounded flight tube of 12-cm length, where they are directed to the detector area (18-mm diameter) by means of an Einzel lens for a maximum transmission efficiency. The detector is a dual chevron microchannel plate assembly (MCP). The time of flight spectra of the emitted anions are obtained using a multistop time-to-digital converter (up to 256 stop signals). Since each cluster impact on the target gives rise to an electron emission that is large enough [8] to generate a signal from the MCP, this signal is used to start the recording of the arrival times of negative ions on the detector.

Since, as shown later on,  $\text{Au}_p^-$  clusters with large  $p$  values are observed in the TOF spectra, the detection efficiency of our setup has to be optimized. To this respect a voltage of +340 V is applied to the front face of the MCP in order to drive the electrons emitted from the interchannel web of the detector back to its surface and so to improve the detection efficiency. Moreover, since the ion-electron conversion is a velocity-dependent process (ion induced kinetic electron emission), the detection efficiency at a given energy is expected to decrease for ions of increasing masses. As a matter of fact, such a dependence of the detection efficiency on the ion impact energy has been observed in our experiments when varying the impact energies between 3.5 and 6.34 keV. For energies above 5.4 keV, the emission yields

are constant for  $Au_p^-$  clusters with  $p$  values between 1 and 6 and increase of only 20-25 % for clusters of intermediate size ( $6 < p \leq 17$ ). Then the detection efficiency has been considered as being at maximum for clusters of size as large as 17. On the other hand, the continuous increase of the yields of larger  $Au_p^-$  clusters with impact energy indicates that the detection efficiency is not at maximum for high-mass ions ( $M > 3300u$ ).

The first qualitative information is clearly appearing in Fig. 1, which shows the TOF spectra of the negative ions emitted from the gold target under the impact of  $Au^+$  ions,  $Au_3^+$  and  $Au_9^+$  clusters of the same velocity ( $E_0 = 150 \text{ keV/atom}$ ). The spectra are normalized to the same number ( $5 \cdot 10^6$ ) of incident Au atoms, hitting the target either as  $Au^+$  atomic ions or as constituent atoms of clusters. Not only the emission of  $Au_p^-$  clusters ( $3 \leq p \leq 17$ ) is larger under impact of clusters than under  $Au_1^+$  impact, but also  $Au_p^-$  clusters of larger sizes ( $p > 17$ ) are observed. This can be seen already in the spectrum obtained with  $Au_3^+$  incident clusters, and more clearly in the spectrum obtained with  $Au_9^+$  incident clusters, with the presence of large clusters, up to  $p$  values above 40. For these most favourable conditions of intense cluster emission, we have been able to detect the presence of doubly-charged anions. Although not shown in the present spectra, the  $Au_{23}^{2-}$ ,  $Au_{25}^{2-}$ ,  $Au_{27}^{2-}$  and  $Au_{29}^{2-}$  clusters are observed free from interference with small amounts of contaminant ions [3]. Note that gold dianionic clusters have been recently observed in experiments of electron attachment to free monoanionic clusters stored in a Penning trap [9] and in laser ablation experiments [10]. Finally, and in sharp contrast with these findings, the intensity of the  $Au_1^-$  peak is systematically lower under cluster impact.

The emission yield  $Y_p(n)$  is the mean number of  $Au_p^-$  anions emitted per impact of a  $Au_n^+$  projectile. The yield values reported below are the measured values. They are not corrected neither for the geometrical efficiency of the MCP which is not absolutely known

(approximately 0.6), nor for the statistical distribution of the number of emitted ions with a given  $p$  value. Assuming a Poisson distribution for the emission would increase the measured yield values of at most 14%. The statistical error on the measured yields, calculated for a  $2\sigma$  confidence limit, is below 1% for small size ions ( $p \leq 9$ ). It continuously increases from 1 to 10% for ions of intermediate size ( $9 \leq p \leq 25$ ) and amounts to  $\sim 50\%$  for the largest ions ( $p \sim 40$ ). The uncertainty is appreciably larger in the measurements performed with  $\text{Au}_1^+$  atomic ions. In this case the statistical error increases from 1 to 10% for small size ions ( $p \leq 7$ ) and reach  $\sim 30\%$  for  $\text{Au}_{17}^-$ .

The cluster effect on the emission yields is shown in Fig. 2, where the values of  $Y_p(n)/n$ , the  $\text{Au}_p^-$  anion yield per atom of the projectile, are displayed as a function of the size  $p$  of the  $\text{Au}_p^-$  anions and for  $n$  values between 1 and 9. The full line curve in the figure corresponds to the statistical detection limit,  $L_D$ , calculated for a 90% confidence level from the background value under the  $\text{Au}_p^-$  peaks in the TOF spectra. Two comments can be made: - i/ The oscillating behavior of the emission yields of odd and even-sized clusters is well observed in the low size region ( $p < \sim 20$ ). Similar observations were reported for gold cluster ions sputtered from gold targets under atomic ion bombardment [11] and laser irradiation [10]. This odd-even effect in the mass distribution of gold anionic clusters reflects the well-known odd-even alternation in electron affinities [12] and consequently in gold anion stability: The binding energy of odd-size anionic clusters (even number of valence electrons) is stronger than that of even-size anionic clusters, because of the pairing energy of valence electrons. - ii/ Except the case of the  $\text{Au}_1^-$  monomer, the emission yields per incident atom increase with the size  $n$  of the incident cluster but the effect tends to saturate at  $n = 7$ . This nonlinear effect is clearly observed for the emission of  $\text{Au}_p^-$  clusters in the low size range up to  $p = \sim 17$ . Beyond  $\sim 17$  atoms, the  $\text{Au}_p^-$  clusters are detected under cluster impact only and

their emission yields tend to a linear dependence upon the projectile size. It is difficult to extend our investigation to clusters of larger size owing to the reduced detection efficiency and the larger statistical uncertainty for high mass ions. Finally it is of interest to compare the number of gold atoms belonging to anionic clusters ( $\sum p Y_p(n)$  with  $p > 1$ ) to the total number of atoms ejected as anions ( $\sum p Y_p(n)$  with  $p \geq 1$ ). This “cluster fraction”, found to be equal to 0.77 for bombardment by  $Au^+$  ions, amounts to 0.94 for  $Au_7^+$  and  $Au_9^+$  clusters, which means that under cluster impact almost all target atoms are ejected as clusters.

A quantification of the cluster effect on the anion yields is obtained by defining the factor  $\varepsilon_p(n,1)$ , such as  $\varepsilon_p(n,1) = Y_p(n) / n Y_p(1)$ , which is, for a given  $p$  value, the emission yield per atom of the incident  $Au_n^+$  clusters, normalized to the emission yield for the  $Au^+$  ions of the same velocity. The normalization procedure is obviously limited to the size range of the  $Au_p^-$  emitted under  $Au^+$  ion impact ( $1 \leq p \leq 17$ ), as shown in Fig. 3. With the exception of the  $\varepsilon_1(n,1)$  and  $\varepsilon_2(3,1)$  values, all other values of  $\varepsilon_p(n,1)$  are above unity and so express a yield enhancement. The  $\varepsilon_1(n,1)$  values for the emission of the  $Au_1^-$  monomer are definitely lower than unity ( $\sim 0.67 \pm 0.06$  on the average) and so reveal a reduction of the monomer emission yield per incident atom. This result is in contrast with previously reported data on the monomer emission from metals by low energy clusters [4,5] Moreover recent molecular dynamics simulations of silicon sputtering by Au and  $Au_2$  projectiles at low energy, have shown that the monomer sputtering yield exhibits a linear dependence on projectile size [13]. Nevertheless, except the case of the monomer emission, the previous authors have reported a nonlinear enhancement of the cluster yields, as presently observed.

The yield enhancement factors increase with the size  $n$  of the impinging cluster and, as expected from the previous discussion, tend to saturate at  $n = 7$ . Such a size limitation of the nonlinear effect has already been observed in secondary electron emission under gold cluster



impact [8]. The largest enhancement factors are  $\varepsilon_5(9,1)$  and  $\varepsilon_7(9,1)$  that are close to 6, which means that the emission yields are more than 50 times higher than those resulting from  $\text{Au}^+$  atomic ion impact. Of course, higher ion emission yields are expected for incident gold clusters of size larger than 9, even if the enhancement factor tends to a constant value.

As for the  $p$  dependence of  $\varepsilon_p(n,1)$  values, two particular effects clearly appear: i/ two distinct size ranges can be distinguished : up to  $p = 7$   $\varepsilon_p(n,1)$  increases with  $p$  and then decreases for larger  $p$  values down to values close to unity. This result suggests that the yield enhancement for large clusters ( $p > 17$ ) tend to present a linear dependence on the projectile size. The collective effect on ion emission seems to vanish. ii/ The odd-even alternation in cluster stability is still observed in the  $\varepsilon_p(n,1)$  values. These features can be explained from metastable decay on the time scale of cluster acceleration (several hundred nanoseconds). Owing to the high density of the energy deposit in the subsurface region of the target at cluster impact, gold clusters leave the solid with much higher internal excitation than for  $\text{Au}^+$  impact. The decay by Au evaporation results in a size distribution that reflects the cluster stability according to their electronic shell structure [14,15]. Thus, the yield enhancement at cluster impact is expected to be lower for the least stable clusters. This explains the smaller enhancement factors observed for even-size clusters and the systematic decrease observed for  $p$  values larger than 7, which corresponds to the filling of a new electronic shell.

In conclusion, as for collisional sputtering the intensity of the anion emission from a gold target under gold cluster impact increases with the projectile size, more than expected from a simple linear effect. The highest values of the yield enhancement are obtained for a projectile size around 7 and then tend to saturate. This enhancement is also observed to vary with the size  $p$  of the emitted clusters, increasing up to a maximum value ( $\sim 6$ ) in the low size region ( $p = 5 - 7$ ), and then decreasing to small values for the largest cluster sizes. Since an

increase of the energy density deposited in the solid leads to the ejection of target clusters with increasing internal energies, cluster cooling by atom evaporation appears as a key factor for the variation of the cluster yield enhancement, the cluster stability being related to their electronic shell structure. Then, it will be of major interest to study the gold cation emission as well as to extend such measurements to non-metallic solids.

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## Figure captions

FIG. 1. Time of flight spectra of gold anions emitted from a gold target under impact of 150 keV/atom  $\text{Au}^+$  atomic ions,  $\text{Au}_3^+$  and  $\text{Au}_9^+$  clusters, respectively. Each spectrum corresponds to  $5 \cdot 10^6$  incident Au atoms (see text). The peaks are labelled with the number of atoms,  $p$ , of the  $\text{Au}_p^-$  emitted anions.

FIG. 2. Variation of the anion emission yield per atom of the incident projectile,  $Y_p(n)/n$ , as a function of the size  $p$  of the anions, for various  $\text{Au}_n^+$  cluster projectiles. The solid line is the statistical detection limit.

FIG. 3. Variation of the factor  $\varepsilon_p(n,1)$  ( $= Y_p(n) / n Y_p(1)$ ) as a function of the size  $p$  of the  $\text{Au}_p^-$  emitted anions for various  $\text{Au}_n^+$  cluster projectiles.

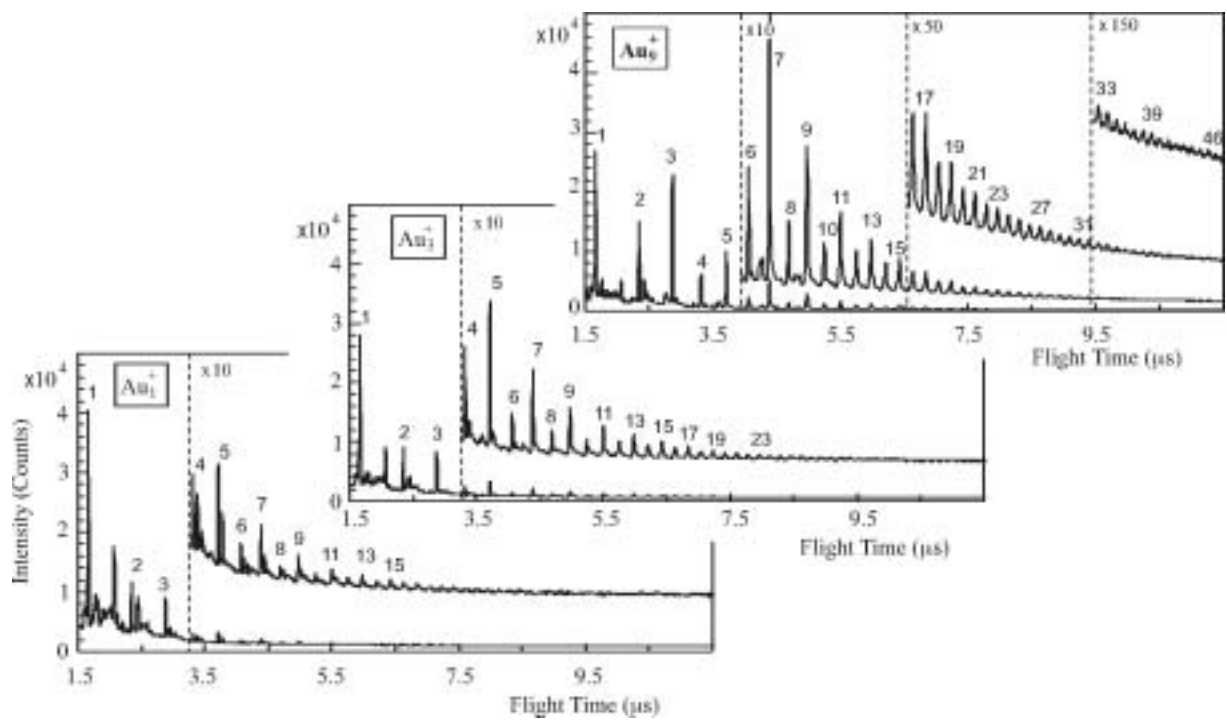


FIG. 1

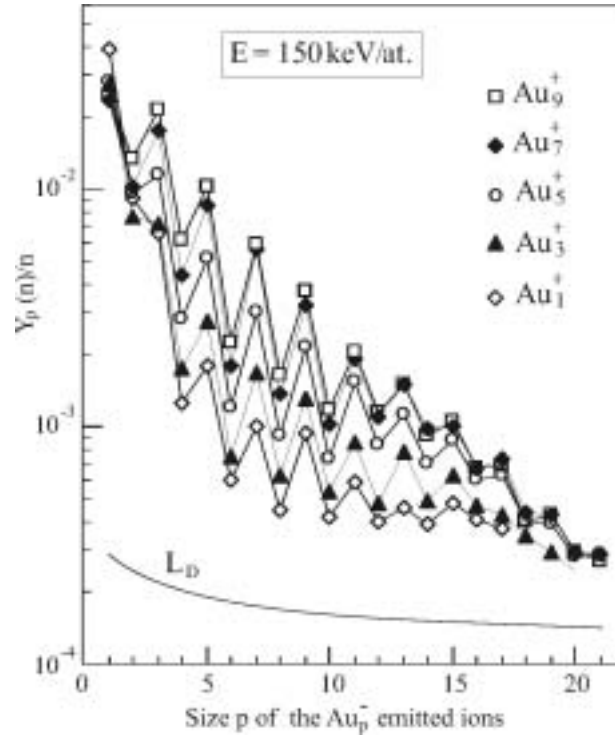


FIG. 2

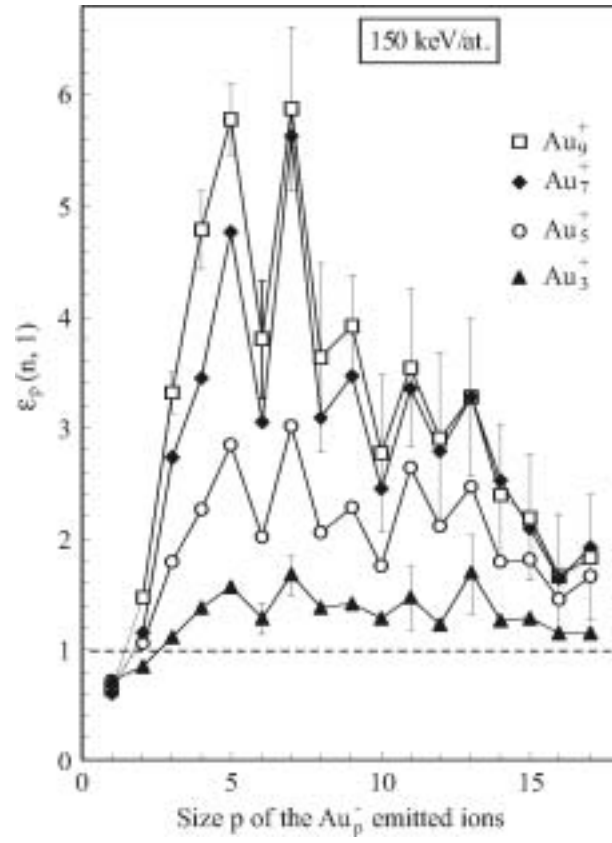


FIG 3