Simultaneous Ejection of Two Molecular Ions from keV Gold Atomic and Polyatomic Projectile Impacts

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We present the first experimental data on the simultaneous ejection of two molecular ions from the impact of Au_n^+ $(1 \leq n \leq 4)$ with energies ranging between 17 and 56 keV. The yields from single phenylalanine (Ph) emission, coemission of two Ph ions, and emission of the Ph dimer were measured. Large increases (1 to 2 orders of magnitude) in coemitted ion yields were observed with increasing projectile energy and complexity. Correlation coefficients were calculated for the coemission of two Ph ions; their behavior suggests differences in emission pathways for bombardment by atomic and polyatomic projectiles.

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Kiloelectronvolt polyatomic projectiles (e.g., Au_n^+, C_{60}^+) have been shown to be very efficient for the ejection of secondary ions from surfaces in comparison to atomic projectiles of the same velocity [1–4]. The enhanced emission of secondary ions has been documented with measurements of the secondary ion yield, i.e., the average number of specified secondary ions produced per polyatomic projectile impact on different targets [5–7]. Several authors have proposed mechanisms that can account for enhanced sputtering and, by implication, enhanced secondary ion emission beyond that expected from the linear collision cascade regime [8–13]. Taken individually, a collision cascade is a stochastic event [14]. This is readily apparent when examining the emission of a molecular ion (a signal useful for chemical analysis). Typically most collision cascades are null events; however, in the subset of productive collision cascades, some can be "superefficient," i.e., they result in the emission of multiple molecular ions. The occurrence of superefficient collision cascades raises two questions. First, what is their rate of production as a function of projectile characteristics? Further, one must wonder if coemissions are due to different pathways in desorption ionization with respect to single ion emission or simply due to random occurrences.

In this study, we present the first experimental data on the simultaneous ejection of two molecular ions as a function of keV projectile characteristics. We report the yields for the coemission of two phenylalanine, Ph, molecular ions, and for comparison those pertaining to the emission of a single Ph molecular ion. Further, we include below data on the emission yield of charged dimers, Ph_2 (condensation product of two molecules).

In addition to the fundamental questions noted above, the study is also of interest from an applied perspective. Coemitted or coincidentally emitted ions imply that they originate from molecules colocated within a surface volume perturbed by a single projectile impact [14]. Indeed, coincidental ion emission provides an approach for the chemical analysis of nanodomains. The relevance for analysis of nanostructures will depend on the effectiveness of the projectile to cause coemission of two or more analytically significant ions.

Gold atomic and polyatomic projectiles Au_n^{m+} $(1 \leq n \leq 4; m = 1, 2)$ were generated using a liquid metal ion source described elsewhere [2]. The energy range studied was between 17 and 56 keV. The experiments were run in the event-by-event bombardment/detection mode. Secondary ions from single projectile impact events were recorded in a linear time-of-flight instrument. In our pulse counting scheme, we cannot detect ion multiplicity, i.e., the simultaneous arrival of two ions with the same mass. To recognize the ejection of two molecular ions, we chose a target that consisted of an equimolar mixture of l-Ph (Aldrich P1, 700-8, $M_w = 165.19$) and deuterated l-Ph (Aldrich 49, 014-8, $M_w = 173.26$). This allows for the detection of two phenylalanine molecular ions, Ph_H $[M\text{-H}]^-$ $(m/e = 164)$ and Ph_D $[M\text{-H}]^-$ $(m/e = 172)$ similar in mass with the same physical characteristics. The mixture of the two phenylalanines was vapor deposited onto a stainless steel support.

A conventional time-of-flight, TOF, mass spectrum of negative ions from 25 keV Au_3^+ bombardment of a Ph target is shown on Fig. 1(a). The yield of the Ph molecules emitted per one n-atom projectile impact, $Y_n(\text{Ph})$, can be calculated from the observed yield of deuterated molecules, $Y_n(\text{Ph}_D)$, by

$$Y_n(\text{Ph}) = Y_n(\text{Ph}_D)/\rho = I_n(\text{Ph}_D)/\alpha N \rho \tau, \qquad (1)$$

where $I_n(\text{Ph}_D)$ is the measured number of emitted molecular ions, α is the ionization probability, N is the number of bombardment events, ρ is the relative concentration of Ph_D ($\rho = 0.5$ for our experiment), and τ is the instrument transmission and detection efficiency,

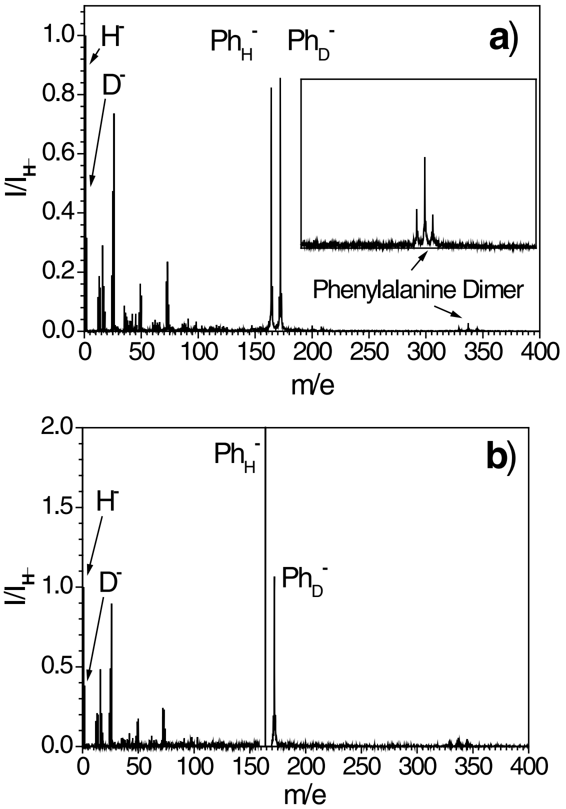

FIG. 1. (a) Negative ion TOF mass spectrum of a Ph_H and Ph_D mixture from 25 keV $Au_3{}^+$ bombardment. The inset is from the molecular dimer region. (b) Negative ion coincidence TOF mass spectrum of all ions coemitted with m/e 164.

constant for all measurements. An analogous expression can be written using the measured number of Ph_H molecular ions.

In Fig. 1(a), we highlight an inset of the molecular dimer region. Three peaks are observed, resulting from the three possible combinations: Ph_H-Ph_H, Ph_H-Ph_D, and Ph_D-Ph_D. Their relative intensities of 1:2:1 reflect a binomial distribution. This is direct evidence that, in our experiment, the Ph_H and Ph_D molecules were homogeneously mixed on the surface.

Figure 1(b) is a "coincidence" TOF mass spectrum of all secondary ions coemitted with the Ph_H molecular ion. This spectrum was collected using coincidence counting techniques described elsewhere [14]. The spectrum in Fig. 1(b) is the sum of individual spectra in which the Ph_H molecular ion was detected. The coincidentally recorded peak of the Ph_D molecular ion indicates that two negatively charged intact molecular ions can be emitted simultaneously, as a result of a single polyatomic projectile impact. The intensity of the Ph_D peak represents the number of coemitted Ph_H and Ph_D molecular ions.

Figure 2(a) shows the yield of Ph molecular ions emitted per projectile. These data confirm previous measurements in this energy range with these types of projectiles [1,2]. Figure 2(b) is a similar plot but now for the yields of two Ph molecular ions (Ph_D and Ph_D) coemitted from a single projectile impact. Figure 3 is a plot of the secondary ion yields for the Ph dimer.

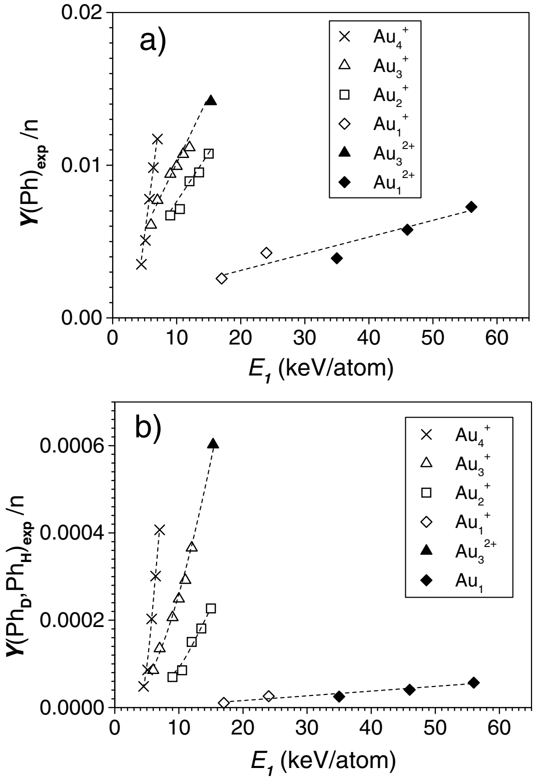

FIG. 2. (a) Secondary ion yields for the Ph molecular ion $(M\text{-H})^-$ on a per atom basis as a function of the energy per atom of the $Au_n{}^{m+}$ projectiles; $n = 1$ to 4, $m = 1$, 2. (b) Secondary ion yields of coemitted Ph_H and Ph_D molecular ions $(M\text{-H})^-$ on a per atom basis as a function energy per atom of the $Au_n{}^{m+}$ projectiles; $n = 1$ to 4, $m = 1$, 2.

The yields can be considered from two viewpoints: the effectiveness of the projectile, and the question of

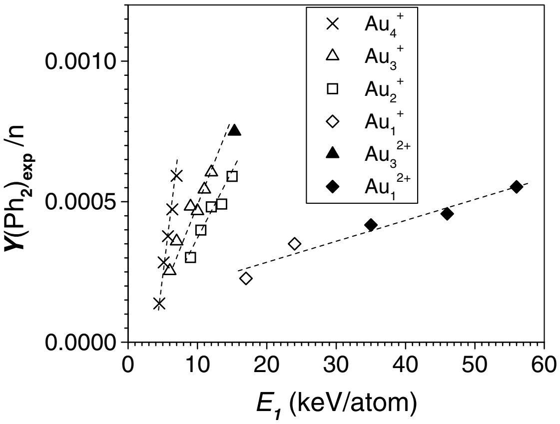

FIG. 3. Secondary ion yields for the Ph dimer ion on a per atom basis as a function of the energy per atom of the $Au_n{}^{m+}$ projectiles; $n = 1$ to 4, $m = 1$, 2.

correlation in the coincidental emission. The effectiveness of an n-atom projectile over the atomic projectile can be expressed in the form of an enhancement factor, $\varepsilon_n = Y_n/nY_1$, where Y_n is the yield from an n-atom projectile and Y_1 is the yield from the atomic projectile [2]. As is shown in Figs. 2 and 3, the yields Y_n depend on both the projectile energy per atom, $E_1 = E/n$, and the number of cluster constituents, n. The dependency of ε_n on these parameters can be expressed as follows: For the coemission of two phenylalanine molecular ions, $\varepsilon_n(\mathrm{Ph_H}, \mathrm{Ph_D}) \propto n^2 E_1^{2/3}$, and, for the emission of the phenylalanine dimer, $\varepsilon_n(\mathrm{Ph}_2) \propto n^2 E_1^{4/3}$. The relatively strong dependence of $\varepsilon_n(\mathrm{Ph}_2)$ on energy is caused by a different energy scaling of $Y_1(\mathrm{Ph}_2)$ and indicates that the pathway for emission of the dimer is different from that of molecular ion emission, involving perhaps the emission of more complex molecular assemblies that decay to the stable dimer configuration. For reference, the enhancement factor for the emission of single phenylalanine ions, $\varepsilon_n(\mathrm{Ph})$, shows an energy dependence of $E_1^{1/3}$ and, within the parameters explored here, is greater than unity; i.e., there is a "cluster effect." In the case for the emission of coincidental molecular ions and that of dimers, the respective values of ε_n are again greater than unity. More importantly, their respective scaling to E_1 shows a magnified cluster effect. This means that those emissions are due to the overlapping of higher energy collision cascades and the creation of spikes which have been shown to be efficient for the emission of large molecules and their dimers [8,10].

To understand if the molecular ion coemission is correlated, we need to calculate the correlation coefficient Q_n [15]. First, we have to establish the relationship between the number of emitted molecular ions and the parameters describing the target composition. The case presented here is for a two-component target and for event-by-event bombardment/detection. Each observation relates to the number of molecules emitted per event, k, and is small enough that the binomial distribution of $\mathrm{Ph_H}$ and $\mathrm{Ph_D}$ molecules must be taken into account. In k emitted molecules, there will be i molecules of $\mathrm{Ph_D}$.

The yield of deuterated molecular ions emitted is expressed as

$$Y_n(\mathrm{Ph_D}) = \sum_k \sum_{i=0}^{k} P_k i \Psi_i = \left(\sum_k k P_k\right)\left(\sum_{i=0}^{k} \frac{i}{k} \Psi_i\right). \quad (2)$$

In the above equation, P_k is the probability that k molecules are emitted, and Ψ_i is the binomial distribution of $\mathrm{Ph_D}$ molecules within k. It may be recalled that Ψ_i is given by $\Psi_i = \frac{k!}{i!(k-i)!} \rho^i (1-\rho)^{k-i}$, with $\sum_{i=0}^{k} \frac{i}{k} \Psi_i = \rho$. The sum $\sum_k k P_k = Y_n(\mathrm{Ph})$ is the total sputtering yield of phenylalanine molecules. Thus, the yield of deuterated, molecular ions $Y_n(\mathrm{Ph_D}) = Y_n(\mathrm{Ph_H}) = \rho Y_n(\mathrm{Ph})$ regardless of the distributions of Ψ_i and P_k.

The situation is different when two phenylalanine molecules are coemitted. In this case, for any given impact the relative abundances of $\mathrm{Ph_H}$ and $\mathrm{Ph_D}$ fluctuate within the random number of k emitted molecules. The yield of coemitted Ph molecules $Y_n(\mathrm{Ph,Ph})$ can be calculated from the measured coemission yields $Y_n(\mathrm{Ph_H,Ph_D})$ as

$$\begin{aligned} Y_n(\mathrm{Ph, Ph}) &= Y_n(\mathrm{Ph_H, Ph_D})/\rho^2 \\ &= I_n(\mathrm{Ph_H, Ph_D})/\alpha^2 N \tau^2 \rho^2 \\ &= \sum_k \sum_{i=0}^{k} (k-1)(i - i^2/k) P_k \Psi_i/\rho^2, \end{aligned} \quad (3)$$

where $I_n(\mathrm{Ph_H,Ph_D})$ is half the measured number of simultaneously emitted $\mathrm{Ph_H}$ and $\mathrm{Ph_D}$ molecular ions as a function of Ψ_i and P_k. One should keep in mind that the detection technique does not discriminate between the coemission events $(\mathrm{Ph_H,Ph_D})$ and $(\mathrm{Ph_D,Ph_H})$, so $I_n(\mathrm{Ph_H,Ph_D})$ represents half of the total number of the detected coincidence events ($\rho = 0.5$).

As can be seen from Fig. 2, the energy of the projectile and the number of constituent atoms affect the yields. We can compare the yields of the single and coemitted molecules using an approach from Ref. [15]. The degree of correlation in the yields of coemitted molecular ions can be described by the experimentally derived correlation coefficient $Q_n(\mathrm{Ph_H,Ph_D})$ [15] defined as

$$Q_n(\mathrm{Ph, Ph}) = \frac{Y_n(\mathrm{Ph, Ph})}{Y_n(\mathrm{Ph}) Y_n(\mathrm{Ph})} = \frac{Y_n(\mathrm{Ph_H, Ph_D})}{Y_n(\mathrm{Ph_H}) Y_n(\mathrm{Ph_D})}. \quad (4)$$

Substitutions from Eqs. (1) and (3) give the expression of Eq. (4) in the form

$$Q_n(\mathrm{Ph, Ph}) = \frac{I_n(\mathrm{Ph_H, Ph_D})}{I_n(\mathrm{Ph_H}) I_n(\mathrm{Ph_D})} N, \quad (5)$$

which shows that $Q_n(\mathrm{Ph, Ph})$ does not depend on α, τ, ρ and can be calculated direct from the experimentally determined values $I_n(\mathrm{Ph_H, Ph_D})$, $I_n(\mathrm{Ph_H})$, $I_n(\mathrm{Ph_D})$, and N.

A plot of experimental values of Q_n versus kinetic energy per projectile atom is shown in Fig. 4. The experimental data can be compared with calculated ones on different yield distributions, P_k [Eqs. (2)–(4)]. The behavior of Q_n indicates that P_k is different for atomic and cluster projectiles. To our knowledge, information describing P_k for the sputtering of intact molecules does not exist in the literature. It may be mentioned that molecular dynamics simulation shows qualitative differences in the sputtering yield distributions of silicon clusters by Au and Au_2 bombardment [10]. This qualitative result indicates that P_k for polyatomic projectiles can be approximated by a symmetrical function, possibly a Poisson-like function. Indeed, the Poisson-like function used as P_k in Eq. (5) models a behavior of Q_n similar to our experimental curve.

For atomic projectiles, a negative binomial distribution is an appropriate approximation for P_k. The behavior of the calculated Q_n is similar to the experimental function

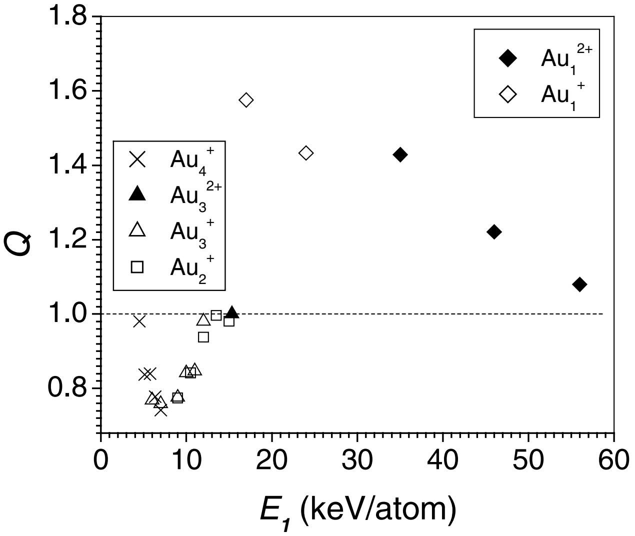

FIG. 4. Q as a function of energy/atom for the selected projectiles in the case of the coemission of two Ph molecular ions. Accuracy in the experimental data is better than ±14% for the atomic projectiles and ±5% for the polyatomic projectiles.

(Fig. 4), when P_k is broad and asymmetric. Surprisingly, a similar distribution was obtained by computer simulation for the sputtering of Ni atoms by Xe^+ ion bombardment [16]. For atomic and polyatomic projectiles, the behavior of P_k differs, indicating different pathways of intact molecular ion emission.

The correlation coefficient Q_n [see Eqs. (4) and (5)] allows for a detailed evaluation of the yields of coemission of two molecular ions to those of single molecular ions eliminating instrumental parameters such as transmission and detection efficiencies. At low bombardment energies (low coincidental ion yields), the different behavior of Q_n for atomic and polyatomic projectiles suggests that respective pathways for the emission of two molecular ions differ. For increasing energies of projectiles (increasing coincidental ion yields), Q_n tends to unity. The asymptotic approach to unity by Q_n for both cases (atomic and polyatomic projectiles) means that $Y_n(\mathrm{Ph_H}, \mathrm{Ph_D}) = Y_n(\mathrm{Ph_D})Y_n(\mathrm{Ph_H})$. The yield of simultaneously emitted molecules $Y_n(\mathrm{Ph_H}, \mathrm{Ph_D})$ is simply a product of the yields for emission of single intact molecules, which means the absence of correlation. Indeed, as the energy increases, yields increase and the influence of fluctuations in the relative densities of the $\mathrm{Ph_H}$ and $\mathrm{Ph_D}$ molecules on the value of $Y_n(\mathrm{Ph_H}, \mathrm{Ph_D})$ decreases.

Our data show large enhancements in the yields of coemitted molecular ions for more complex projectiles. For example, at ~15 keV/atom, the coincidental phenylalanine yields are 50 to 100 times larger for Au_2^+ and Au_3^+, respectively, than for Au^+. The enhanced yields point to a concomitant increase in contribution from superefficient collision cascades. Their occurrence as a function of a range of keV projectile characteristics and of different physical and chemical environments at the desorption site needs to be further explored.

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