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Influence of massive projectile size and energy on secondary ion yields from organic surfaces

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Abstract

We investigated the influence of the projectile size and energy using Au_n^{q+} clusters ($5 < n < 400$, $1 < q < 4$) impacting on a glycine target with a $19q$–$34q$ keV energy range. We show that both CN^- fragment and Gly^- molecular ion yields are equivalent for projectiles with $n > 9$ and increase with the energy per projectile atoms. A maximum yield of 0.5 (50%) for both CN^- and Gly^- was obtained with the Au_{400}^{4+} projectile at 136 keV total energy. For Gly^-, the yield enhancement is linear for Au_n when $n > 5$. Trends for the CN^- fragment are different. A nonlinear yield enhancement proportional to n^3 is observed for Au_n when $n < 9$.

Keywords: Secondary ion emission; Gold massive projectile; Ion yield

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1. Introduction

A number of studies have demonstrated the effectiveness of cluster projectiles for generating secondary ions from organic molecules. These observations made mostly with small polyatomic projectiles (e.g. Au_n, Bi_n with $2 < n < 5$ and C_{60}) are now leading to the application of cluster-SIMS for imaging analysis of biological specimens [1]. However, the projectile characteristics required to maximize the analytical signal from organic molecules (MW up to 2000 Da) in biological specimens remain unclear.

The purpose of this study was to investigate the influence of the projectile size and energy on the yield of ions ejected from an organic target. Gold clusters Au_n^{q+} produced from a liquid metal ion source (LMIS) with a large range of size, $1 < n < 400$, were used as projectiles on glycine as a target. CN^- fragment and Gly^- molecular ion yields were measured for various total impact energies of the projectile ($19q$–$34q$ keV) on the target. These impact energies are typically accessible in SIMS instruments. Recently, similar studies with small gold clusters ($1 < n < 7$) have been reported by Nagy et al. [2] on various organic targets like polystyrene, irganox and phenylalaline targets. Peptide ($500 < MW < 2000$) ion yields obtained from the impact of Au_3^+, Au_5^+, Au_9^+ and Au_{400}^{4+} clusters have been reported for a limited set of projectile energies by Tempez et al. [3] and Novikov et al. [4]. To our knowledge, there are no data on polyatomic projectile characteristics versus yield for CN^-. This species is a preferred signal in conventional ion imaging of biological specimens [5,6].

2. Experimental

The experimental procedure used is that of SIMS with key differences: the nature of the projectile, the bombardment with individual projectiles each resolved in time and space, and the corresponding event-by-event detection of the secondary ions (SIs).

A description of the experimental setup including the Wien filter for projectile selection, pulsing for single impact experiments, ToF mass spectrometer, data acquisition and analysis software for SI identification is provided elsewhere [7]. Details of the operational conditions of the LMIS to produce massive Au clusters, such as "Au_{400}^{4+}" are available in the article by Bouneau et al. [8]. The experiments were performed with four different (10, 15, 20 and 25 kV) extraction voltages of

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the projectile and a −9 kV biased target. Samples were prepared by vapor deposition of glycine powder purchased from Aldrich Inc., on a silicon wafer. The thickness of glycine after vapor deposition was ~5 μm.

3. Results and discussion

The mass spectra of the negative secondary ions obtained from the impact of Au_5^+ and Au_{400}^{4+} on a glycine target are shown in Fig. 1a and b, respectively. The total impact energy of the projectiles on the target was 34q keV. The peak intensity was normalized to the total number of collected events. Peaks of Gly_n with $1 < n < 4$ are clearly observed in both mass spectra. Their intensities are four-fold larger with Au_{400}^{4+}. Many additional peaks corresponding to Au adduct ions are present in Fig. 1b. None were generated with Au_5^+ bombardment (Fig. 1a). Similar observations of Au-adduct ions from Au_{400}^{4+} impacts have been reported on different types of targets [9]. There is an important difference in the relative intensities of CN^- and Gly^- ions from Au_5^+ and Au_{400}^{4+} bombardment. More CN^- ions are produced relative to Gly^- with Au_{400}^{4+}, while this trend is inversed with Au_5^+. This suggests that more fragmentation occurs in the case of Au_{400}^{4+} in addition to the ability of this projectile to produce large amounts of molecular ions. The high intensity of this fragment obtained with Au_{400}^{4+} is of interest for SIMS analysis of biological samples since CN^- is produced from most organic tissues. Indeed, as noted earlier this ion is a routine signal in conventional SIMS of biological specimens.

A systematic investigation of CN^- and Gly^- ion yields was conducted for a suite of Au_n^{q+}, $n = 400, 300, 200, 100$ ($q = 4$), 9 and 5 ($q = 1$) in a 19q–34q keV total impact energy range. Yields are calculated from the area under the peak of interest and normalized to the total number of projectiles used to generate the mass spectra. The yields of both CN^- and Gly^- are reported as a function of the energy per projectile in Fig. 2. Both CN^- and Gly^- yields increase dramatically with the impact energy especially for massive Au clusters in the energy range considered here. Maximum yields of 0.5 were obtained for both CN^- and Gly^- with the Au_{400}^{4+} projectile. The figure shows that for a series of projectiles, Au_n ($n = 9$–400), the CN^- and Gly^- yields are similar for practical bombardment conditions (combination of projectile size and velocity). Note that the behavior of CN^- and Gly^- yields obtained with Au_n^{4+} ($n = 200$–400) at the lowest impact energies differ from those observed at higher energies. The yields for Gly^- are higher than those for CN^-. This trend suggests the existence of a threshold in the energy per atom required in the cluster projectile for the production of CN. Finally, for Au_5^+ a large yield difference is observed: the Gly^- yields are two times larger than those for CN^- for impact energies of 190–340 eV/Au.

Nonlinear effects, i.e. SI yield enhancements, can be examined by dividing the CN and Gly ion yields by the number

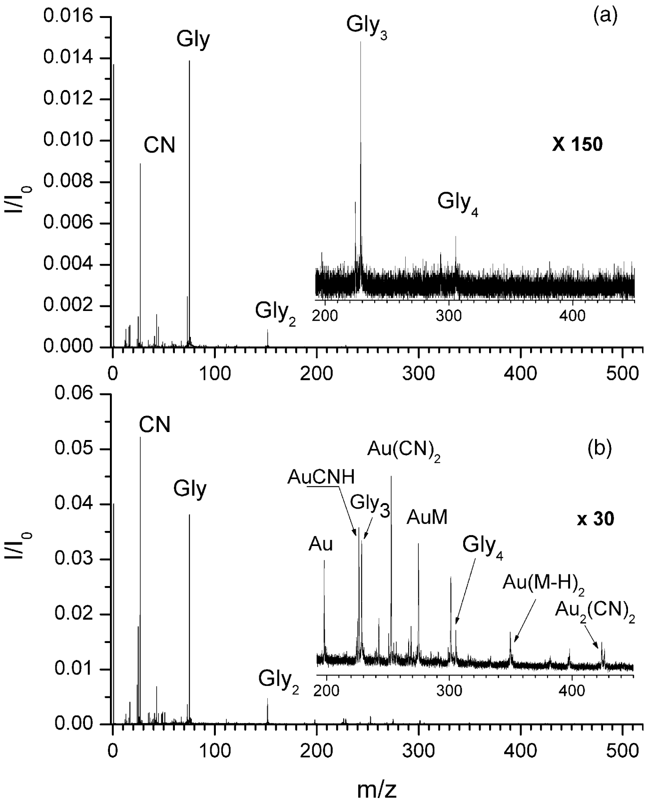

Fig. 1. Mass spectra of the secondary ions produced from the impact of (a) Au_5^+ (total $E = 34$ keV) and (b) Au_{400}^{4+} (total $E = 136$ keV) projectiles on a glycine target.

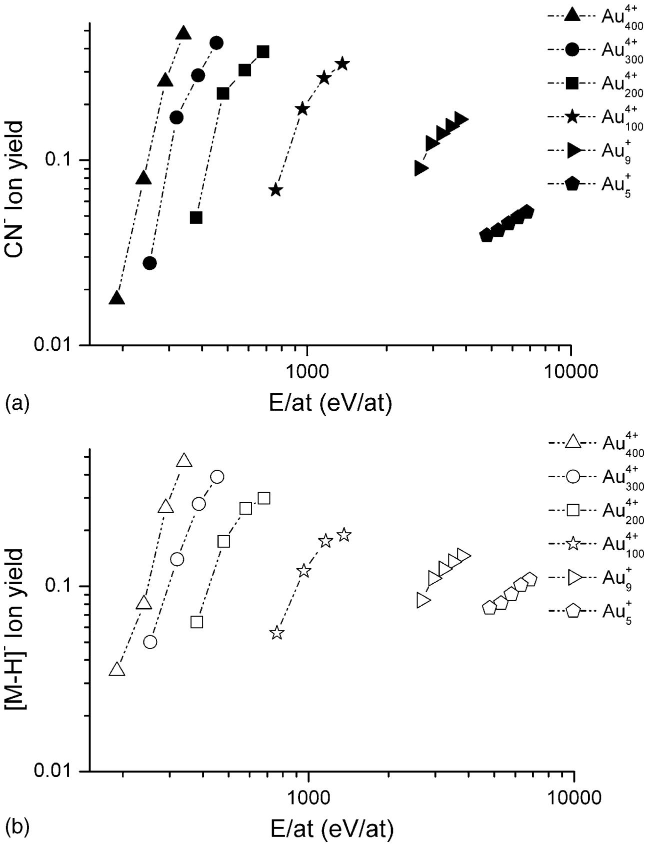

Fig. 2. CN^- fragment ion (a) and glycine molecular ion (b) yields for various Au_n^{q+} ($n = 400, 300, 200, 100, 9$ and 5) in a 19q–34q keV energy range for each projectile.