



Molecular cluster emission in sputtering of amino acids by argon gas-cluster ions



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ABSTRACT

Ten pure amino acid specimens (alanine, arginine, asparagine, glutamine, glutamic acid, isoleucine, leucine, phenylalanine, threonine, and tyrosine) and three binary mixtures (phenylalanine/tyrosine, phenylalanine/arginine, and arginine/tyrosine) were bombarded by 10 keV argon gas-cluster ions Ar_{1000}^+ and the sputter-induced emission of positive secondary ions was investigated by orthogonal time-of-flight secondary ion mass spectrometry (TOF-SIMS). A prolific flux of protonated molecular cluster ions $(M_n + \text{H})^+$ was observed, with up to $n = 22$ for alanine. In most cases, the cluster yields Y_n were found to follow an overall exponential decay with cluster size n , $Y_n \propto \exp(-\beta n)$, although a non-monotonous decrease was found for some clusters. The parameter β varies between ~ 0.2 and ~ 0.65 for the different amino acids; it seems to scale inversely with the respective sputtering yields of the materials. Generally, the yields of dimers relative to monomers are surprisingly high, amounting to 20–170% whereas those of trimers and tetramers are in the range of 10–90%. In amino acid samples with an (unintentionally) enhanced Na content, Na-cationized cluster $(M_n + \text{Na})^+$ were found in addition to $(M_n + \text{H})^+$. For both molecular cluster species the yields exhibit a very similar dependence on the cluster size n . From the binary mixtures, the emission of both homo- and heteromolecular clusters was observed; their size distributions seem to indicate that the two components were not homogeneously distributed within the samples.

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1. Introduction

In secondary-ion mass spectrometry (SIMS) [1,2], the use of cluster ions as projectiles instead of the more common atomic ions has become widespread in recent years (see, e.g. [3–6]). This development was primarily caused by the observation that intact molecular ions could be sputtered from organic and biological samples even at fluences far above the static limit, i.e. beyond the *low-fluence* regime for which each impinging ions impacts onto an undisturbed surface area [2]. In particular, the application of Ar_x^+ gas-cluster ions (with x up to several 1000) has increased dramatically and several reports on their successful use in SIMS have been published in the past decade [7–20]. Specific studies have demonstrated that argon cluster bombardment of organic solids

may lead to a *soft* emission process so that large intact molecules or even molecular clusters can be desorbed (sputtered) from the surface while the fraction of fragmenting species would be small [21–27]. This finding was corroborated by molecular dynamics (MD) computer simulations [28–30]. In addition, MD simulations have illustrated quite impressively (some of) the emission scenarios that might occur under (argon) cluster bombardment of solids [31,32]. As compared to atomic ion irradiation the yields of sputtered species seem to generally increase (sometimes pronouncedly) under cluster impact whereas the number of emitted fragment molecules is reduced, to the extent that depth profiling of (thick) organic and biological layers and 3D imaging became feasible (see, e.g. [33–37]).

While the emission of (large) intact organic or biological molecular ions thus was substantially advanced, the possible ejection of molecular cluster species, i.e. moieties composed of a certain number of the molecules present at the surface has not been studied in detail [38,39]. This is somewhat surprising as the sputtering of

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clusters from elemental and inorganic specimens has been investigated extensively [40,41]. The emission of molecular cluster from amino acids had been noted already in a previous study [26] but a more specific investigation was limited then by the mass resolution and sensitivity of the set-up used. More recently, a prolific cluster emission from phenylalanine was observed [42], exhibiting an abundant flux of protonated molecular cluster ions $(M_n+H)^+$ with $n \leq 12$. An MD simulation of phenylalanine sputtering by Ar_{1000} cluster bombardment also demonstrated the emission of (very) large phenylalanine cluster [43], showing even the formation of a cluster composed of 38 phenylalanine molecules.

In order to examine whether the emission of large cluster species is a general phenomenon and is occurring also for other amino acids, in the present work Ar_{1000}^+ cluster ions were used to study the cluster emission from ten pure amino acid specimens and three binary mixtures. Depending on their abundance, such cluster of molecular species could play an important role in the analysis of materials and, therefore, may warrant a closer examination. In addition, such an investigation may shed light on the emission process which is still not well understood.

2. Experimental

The experiments were carried out in a new custom-built SIMS instrument in the group of Jiro Matsuo at Kyoto University [44,45] which consists of a gas cluster ion source and primary beam line and an orthogonal-acceleration time-of-flight mass spectrometer (TOF-MS) for the detection of sputtered secondary ions. In the ion source, neutral Ar clusters are formed by the supersonic expansion of a high-pressure gas (~ 0.35 MPa) through a nozzle (0.1 mm diameter) and are then introduced into the ionizing chamber. The neutral Ar clusters are ionized by electrons from a hot filament (electron energy 300 eV). Similar to a previous gas-cluster ion beam apparatus [46–48], ionized Ar_x^+ clusters (with x being the number of Ar atoms) are extracted towards the target by accelerating voltages of up to 15 kV. For these settings, the source produces an asymmetric size distribution of Ar_x^+ cluster ions which ranges from $x \sim 500$ to $x \sim 4000$ and exhibits a full-width at half maximum of ~ 1500 ; this distribution has a mean value of $x \sim 1000$. In the following we therefore refer to this beam as Ar_{1000}^+ ions, but no further size selection was carried out in the present study, contrary to our previous work [26,27].

The measurements were done using an ion impact energy of 10 keV. The cluster beam hits the target at an incidence angle of 45° and the ion current was 40 pA; it was scanned across an area of $500 \mu\text{m} \times 500 \mu\text{m}$. Secondary ions emitted under an angle of 45° are detected. Mass spectra were acquired for 100 s which corresponds to 2.5×10^{10} Ar_x^+ ions, resulting in a total ion fluence of 1×10^{13} Ar_x^+ ions/cm².

The detection of ions sputtered from the sample was performed in an orthogonal time-of-flight mass spectrometer (TOF-MS) which is part of a commercial system (JMS-T100LC AccuTOF manufactured by JEOL Ltd.). It employs an rf-only quadrupole ion guide for the transport of secondary ions to the entrance of the TOF proper and enables the efficient transmission of ions in a wide m/z range by focusing them to the optical axis [49]. The mass analyzer is an orthogonal acceleration TOF-MS [50,51], incorporating a 2-stage acceleration and a single-stage reflectron. Ions that have passed through the MS are recorded by means of a microchannel plate detector.

A mass calibration was performed before each analytical run employing a specimen of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) which exhibits a number of quite distinct mass peaks (at m/z 184.1, 790.6, and 1580.2). In this way, a mass accuracy of $\sim 10^{-4}$ was achieved in the mass spectra. The mass

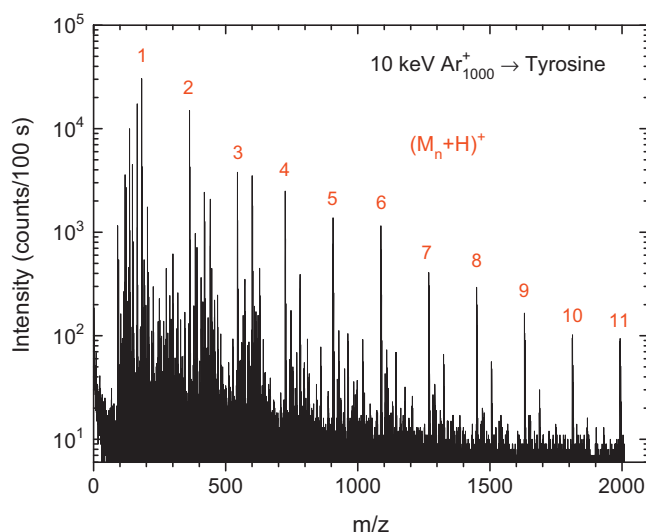


Fig. 1. Mass spectrum from the tyrosine sample under 10 keV Ar_{1000}^+ cluster ion bombardment. The protonated molecular ion $(M+H)^+$ and tyrosine cluster species $(M_n+H)^+$ ($1 \leq n \leq 11$) are labeled.

resolution obtained under these conditions was $M/\Delta M_{FWHM} \sim 5000$ [18,20].

Samples of ten pure amino acids were studied: alanine ($C_3H_7NO_2$), arginine ($C_6H_{14}N_4O_2$), asparagine ($C_4H_8N_2O_3$), glutamine ($C_5H_{10}N_2O_3$), glutamic acid ($C_5H_9NO_4$), isoleucine ($C_6H_{13}NO_2$), leucine ($C_6H_{13}NO_2$), phenylalanine ($C_9H_{11}NO_2$), threonine ($C_4H_9NO_3$), and tyrosine ($C_9H_{11}NO_3$). In addition, three binary mixtures of amino acids (phenylalanine/tyrosine, phenylalanine/arginine, and arginine/tyrosine) with equal amounts of the two components were used. Specimens were prepared as aqueous solutions with a concentration of 0.2 g/L (~ 0.1 g/L was used for arginine and the mixed samples). From these solutions, drops of 50 μL were applied onto the surface of 1 cm \times 1 cm pieces of Si wafers which had been thoroughly cleaned before deposition. Upon drying, this procedure resulted in surface areas of ~ 5 mm diameter covered with the respective amino acid(s). For each amino acid sample several mass spectra were recorded across these surface areas to check the reproducibility and to avoid any inhomogeneity within the deposits.

3. Results and discussion

3.1. Cluster emission from amino acid specimens

The aim of the present work was the investigation of the characteristics of cluster emission from amino acids under gas cluster-ion bombardment. Fig. 1 displays a mass spectrum obtained from the tyrosine sample under 10 keV Ar_{1000}^+ cluster bombardment (mass spectra up to $m/z \sim 2000$ can be recorded in the present experimental set-up). The spectrum shows the presence of the protonated molecular ion $(M+H)^+$ of tyrosine (m/z 182.2). The peaks at lower masses can be assigned to the immonium species of tyrosine (m/z 136.1) and to fragments (m/z 147.1 and 165.1). For higher masses a distinct pattern of mass peaks is observed that are due to the emission of protonated tyrosine cluster ions $(M_n+H)^+$ with $n \leq 11$. (Fig. 1 indicates that even larger clusters might be present in the sputtered flux but the limit of the mass range accessible prevents their detection.) Apart from the $(M_n+H)^+$ cluster ions the mass spectrum exhibits very few other species; the most prominent ones are cluster of the type $(M_n+X)^+$ with $X \sim 57$ u, in particular $(M_3+57)^+$. This observation of an abundant emission of cluster indicates that there is little fragmentation and, hence, that the tyrosine cluster

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