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Energy distributions of atomic and molecular ions sputtered by C_{60}^+ projectiles

A. Delcorte *, C. Poleunis, P. Bertrand

PCPM, Université catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

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Abstract

In the process of investigating the interaction of fullerene projectiles with adsorbed organic layers, we measured the kinetic energy distributions (KEDs) of fragment and parent ions sputtered from an overlayer of polystyrene (PS) oligomers cast on silver under 15 keV C_{60}^+ bombardment. These measurements have been conducted using our TRIFT^{TM} spectrometer, recently equipped with the C_{60}^+ source developed by Ionoptika, Ltd. For atomic ions, the intensity corresponding to the high energy tail decreases in the following order: $C^+(E^{-0.4}) > H^+(E^{-1.5}) > Ag^+(E^{-3.5})$. In particular, the distribution of Ag^+ is not broader than those of Ag_2^+ and Ag_3^+ clusters, in sharp contrast with 15 keV Ga^+ bombardment. On the other hand, molecular ions (fragments and parent-like species) exhibit a significantly wider distribution using C_{60}^+ instead of Ga^+ as primary ions. For instance, the KED of Ag-cationized PS oligomers resembles that of Ag^+ and Ag_n^+ clusters. A specific feature of fullerene projectiles is that they induce the direct desorption of positively charged oligomers, without the need of a cationizing metal atom. The energy spectrum of these PS^+ ions is significantly narrower then that of Ag-cationized oligomers. For characteristic fragments of PS, such as $C_7H_7^+$ and $C_{15}H_{13}^+$ and polycyclic fragments, such as $C_9H_7^+$ and $C_{14}H_{10}^+$, the high energy decay is steep ($E^{-4} - E^{-8}$). In addition, reorganized ions generally show more pronounced high energy tails than characteristic ions, similar to the case of monoatomic ion bombardment. This observation is consistent with the higher excitation energy needed for their formation. Finally, the fraction of hydrocarbon ions formed in the gas phase via unimolecular dissociation of larger species is slightly larger with gallium than with fullerene projectiles.
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1. Introduction

Kiloelectronvolt fullerene ion (C_{60}^+) beams are now available and easy to operate, since the elaboration of a reliable, long lifetime source by the combined efforts of the UMIST surface analysis group and Ionoptika, Ltd. [1]. Buckminsterfullerene ions induce a two order of magnitude enhancement of the parent and fragment ion yields in static secondary ion mass spectrometry (SIMS) of bulk organic materials such as PS oligomer, Irganox 1010 spin-coated films and adsorbed protein layers [1–3]. In the case of PS films, positively charged oligomers are directly desorbed, without the need of a cationizing metal atom. The yield increase observed upon bombardment of metallic samples and thin overlayers on metals appears less significant. For silver surfaces, ion yield enhancement factors of 3.7, 12.5 and 25 have been measured by Sun et al. for Ag^+, Ag_2^+ and Ag_3^+, respectively [4]. For molecular overlayers on the same substrate, MD simulations confirm a sputtering yield enhancement of a factor of two at the most for benzene molecules [5]. These yield enhancement factors indicate a different dependence of the sputtering and ionization probabilities – and probably mechanisms – on the type of target material upon Ga^+ and C_{60}^+ bombardment.

The specific physics at play with fullerene projectiles is now closely scrutinized, with the help of careful experiments and molecular dynamics simulations [6]. For silver targets and benzene overlayers on silver, it has been found that C_{60} molecules transfer their energy in the top surface layers, creating an overheated nanovolume that relaxes via collective atomic and molecular motions, including pressure pulses [5].

In this study, we report the kinetic energy distributions of atomic and molecular ions sputtered by 15 keV C_{60}^+ projectiles. These distributions constitute starting material for future

* Corresponding author.
E-mail address: delcorte@pcpm.ucl.ac.be (A. Delcorte).

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investigations of the desorption mechanisms induced by keV fullerene ions in organic layers.

2. Materials and methods

2.1. Samples

Samples of polystyrene (PS, M_w = 590 Da; M_n = 550 Da) were dissolved in toluene, to a concentration of 0.1 mg/mL. The dissolved molecules were cast on 0.5 cm^2 silver foils by depositing a droplet of the solution on the supports and allowing the solvent to evaporate. Prior to organic sample deposition, all of the Ag substrates were etched for 15 s in H_2SO_4 (60 wt.%) and rinsed in ultrapure water (millipore), 2-propanol and hexane (p.a. grade; Vel).

2.2. Secondary ion mass spectrometry

The secondary ion mass analyses were performed in a PHI-EVANS time-of-flight SIMS (TRIFT 1) [7]. The experimental setup has been described in detail elsewhere [8]. To improve the measured intensities, the secondary ions were postaccelerated by a high voltage (7 kV) in front of the detector. Because of the limited thickness of the molecular coating, no charge compensation was needed. The 15 keV-Ga^+ beam was obtained from a FEI 83-2 liquid metal ion source (1.2 nA dc current; 22 ns pulse width bunched down to 1 ns). The 15 keV-C_{60}^+ measurements were conducted using a primary ion beam system (IOG-C60-20) from Ionoptika Ltd. (2–100 pA dc current with apertures of 300–1000 μm and a 50 V grid voltage). The contribution from C_{60}^{2+} was eliminated by a set of blanking plates. The repetition rate was 8 kHz for the mass range 0–2 kDa. The primary ion current was measured in a small aperture of the sample holder, with and without a positive bias of 27 V (to cancel the effects of secondary electron emission). For the KED measurements, the secondary ions were accelerated by a $(3 + \Delta)$ kV potential applied on the sample. The different energy windows were selected by adjusting the value of Δ and slicing the energy-dispersed secondary ion beam by a 100 μm slit placed at the crossover following the first electrostatic analyzer (1.5 eV passband). With this procedure, a 1 V increase of Δ corresponds to a 1 eV decrease of the energy window defined by the slit. About 45 mass spectra (180 s acquisition time each) were recorded in the mass range 0–2000 Da over a 180 μm × 180 μm area (2.4×10^8 ions per spectrum for Ga^+; 7.2×10^6 ions per spectrum for C_{60}^+). During these experiments, the sample was moved to a fresh area every five spectra to avoid possible degradation effects (especially with Ga^+).

3. Results

3.1. Energy distribution of atomic and cluster ions

The energy spectra of inorganic and organic ions emitted from an overlayer of polystyrene oligomers on metal under kiloelectronvolt gallium ion bombardment have been reported in previous articles [9,10]. For the present study, they were measured again using the same ToF-SIMS apparatus and acquisition parameters to make sure that no instrumental artifact could affect the results obtained under fullerene projectile bombardment. The agreement between the recent measurements and the previously recorded data is very satisfying and it shows that the resolution of the energy-selecting slit has not changed over the years. The energy distributions of Ag^+ sputtered with C_{60}^+ and Ga^+ primary ions are reported in Fig. 1a (semi logarithmic scale). The distribution observed under Ga^+ bombardment is broad, with a high energy tail extending beyond 80 eV. The tail of the distribution exhibits a clear E^{-2} dependence beyond 10 eV, such as that expected for atoms sputtered in the linear collision cascade regime. In contrast, Ag monoatomic ions desorbed by C_{60}^+ projectiles have a much narrower KED with a high energy decay close to $E^{-3.5}$. The negative apparent energy part of the distribution (higher sample voltage) also indicates that a significantly larger fraction of Ag^+ ions are produced by unimolecular dissociation in the gas phase [11] using fullerene projectiles. The comparison with atomic ions sputtered from the polystyrene molecular overlayer, Fig. 1b, indicates a different behavior. The distributions of C^+ and H^+ are decaying very slowly with increasing energy (C^+: $E^{-0.4}$ – H^+: $E^{-1.5}$), much like the same ions sputtered by Ga^+ projectiles. Under kiloelectronvolt atomic ion bombardment, sputtered metallic clusters usually exhibit steeper energy dependences than monoatomic metal ions, as do their neutral homologues. Clusters ejected from the silver substrate of our sample by 15 keV Ga^+ are not an exception (see for example Ref. [9]). In contrast, the KEDs of Ag monoatomic ions and Ag clusters (Ag_2^+, Ag_3^+) emitted by C_{60}^+, Fig. 1c, are very similar. All these observations indicate that the emission processes of ions sputtered from the metallic substrate of the sample drastically change when going from 15 keV Ga^+ to 15 keV C_{60}^+ primary ion bombardment. These fundamental differences are tentatively interpreted in Section 4 of the article.

3.2. Energy distribution of molecular ions

One of the strengths of the TRIFT instrument is that the KEDs of all the secondary ions present in the mass spectrum are recorded in parallel. Therefore, the KED measurement provides a wealth of information that cannot be exhaustively described in a progress report like this one. The choice made here is to show a small number of KEDs, in order to illustrate the emission properties of some characteristic ions of the polystyrene mass spectrum. The KEDs of the molecular ion, the Ag-cationized molecule and two fragments desorbed from polystyrene under Ga^+ and C_{60}^+ bombardment are plotted in Fig. 2. In contrast with atomic silver ions, the KEDs of polystyrene ions are all significantly broader using C_{60}^+ projectiles. The slope of their high energy tail varies from $\sim E^{-3.5}$ (Ag-cationized molecule) to $\sim E^{-8}$ ($C_7H_7^+$). A specific feature of fullerene projectiles is that they induce the direct desorption of positively charged oligomers, without the need of a cationizing metal atom. The energy spectrum of these PS tetramer ions is significantly

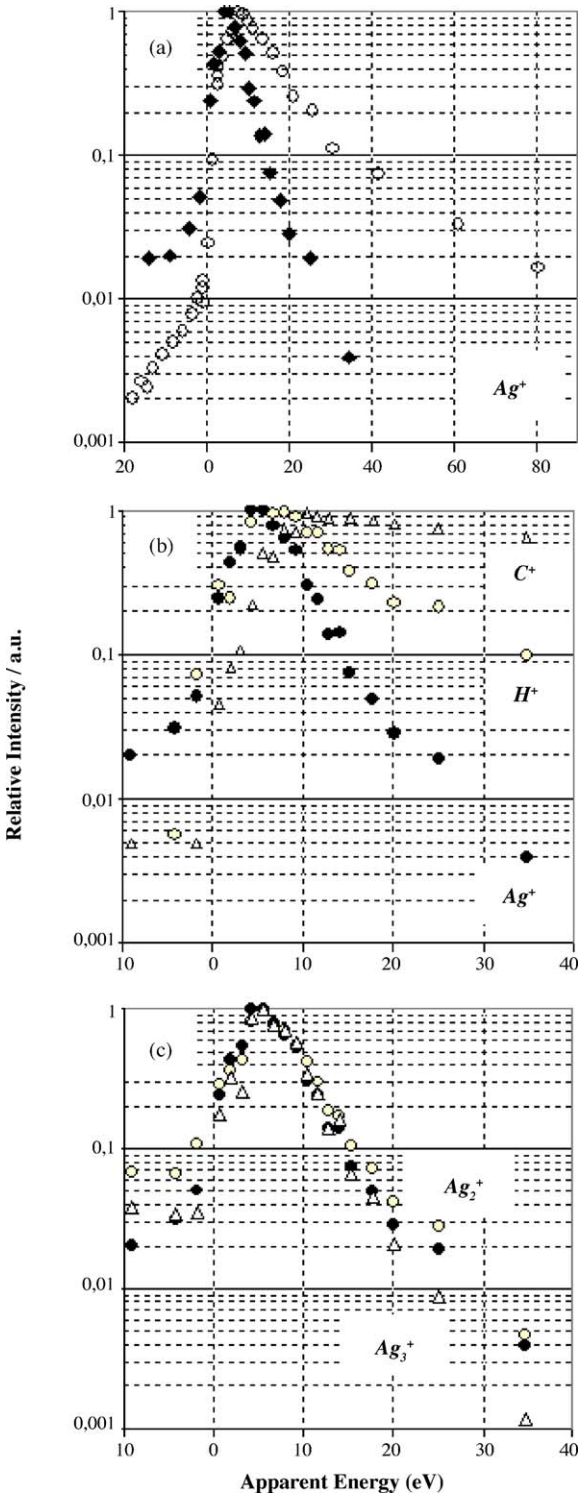

Fig. 1. Energy distributions of atomic and metal cluster ions sputtered from a polystyrene overlayer cast on silver. (a) Ag^+ sputtered by 15 keV Ga^+ (open circles) and by 15 keV C_{60}^+ projectiles (full diamonds); (b) C^+ (open triangles), H^+ (open circles) and Ag^+ (full circles) sputtered by 15 keV C_{60}^+ projectiles; (c) Ag^+ (full circles), Ag_2^+ (open circles), Ag_3^+ (open triangles) sputtered by 15 keV C_{60}^+.

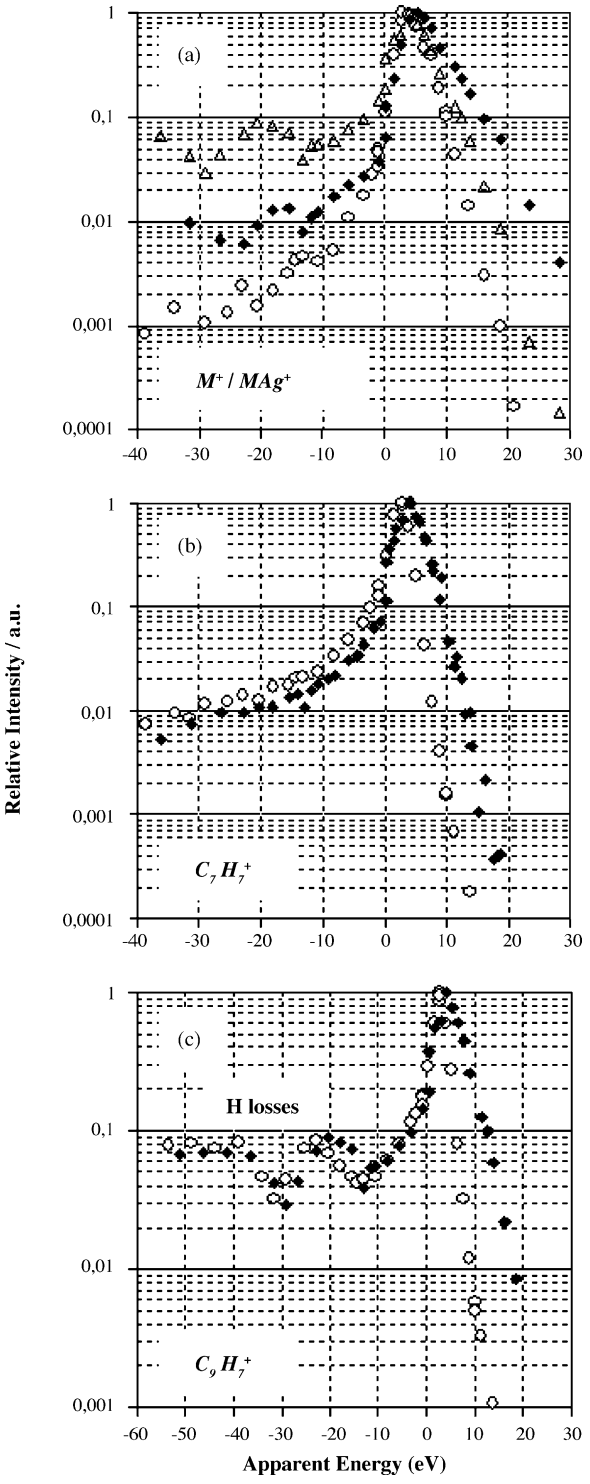

Fig. 2. Energy distributions of molecular fragment and parent-like ions sputtered from a polystyrene overlayer cast on silver. (a) Polystyrene tetramer ions sputtered by 15 keV C_{60}^+ projectiles (open triangles) and Ag-cationized polystyrene tetramers sputtered by 15 keV Ga^+ (open circles) and by 15 keV C_{60}^+ projectiles (full diamonds); $C_7H_7^+$ (b) and $C_9H_7^+$ (c) PS fragment ions sputtered by 15 keV Ga^+ (open circles) and by 15 keV C_{60}^+ projectiles (full diamonds).

narrower then that of Ag-cationized molecules, a trend that was also observed for other polycyclic molecules under Ga^+ bombardment [9] but could not be verified for polystyrene because molecular ions were not formed in these conditions.

The question of the internal energy of molecular/fragment ions desorbed by buckminsterfullerenes has been raised in the SIMS community. Higher internal energies should cause a larger number of metastable decay reactions, i.e. one should observe a

larger intensity in the negative apparent energy part of the KEDs [11]. Fig. 2a indicates that, for parent-like ions, the ratio R = [yield of fragments formed in the vacuum/yield of fragments formed at the surface], i.e. the integral of the negative part of the distribution divided by the integral of the positive part of the distribution, follows the order $R_{C_{60}^+}(M^+) \gg R_{C_{60}^+}(MAg^+) \approx R_{Ga^+}(MAg^+)$. This observation suggests that the dissociation of MAg_n^+ aggregates in flight might be an important formation channel for M^+ under fullerene ion bombardment. Looking at the peak normalized KEDs of $C_7H_7^+$ and $C_9H_7^+$, it is not clear that Ga^+ and C_{60}^+ induce qualitatively different metastable decay reactions for PS fragments. First, the slope of the curves corresponding to unimolecular dissociation in the acceleration section of the spectrometer is similar. Second, the structure in the negative part of the distribution of $C_9H_7^+$ (but also $C_{10}H_8^+$; $C_{14}H_{10}^+$ and other polycyclic ions) is observed with both projectiles. The horizontal shift of the single H loss peak towards higher energies is an effect of the widening of the distributions under fullerene projectile bombardment. Quantitatively, the fractions of fragment ions produced by metastable decay in the gas phase are larger with Ga^+ projectiles. For $C_7H_7^+$ and $C_9H_7^+$, the ratio R is roughly two times larger for Ga^+ than for C_{60}^+ bombardment. This difference is more directly observed with a normalization procedure that involves the integral of the positive part, rather than the peak height of the distributions (not shown).

4. Discussion and conclusion

The data collected in this contribution can be interpreted with the help of complementary observations and concepts developed in recent studies of fullerene projectile-induced sputtering. Experimentally, Sun et al. measured the KEDs of neutral Ag atoms and dimers sputtered from an HNO_3-etched silver sample [4]. They observed that, under C_{60}^+ bombardment, the KED of silver dimers was slightly broader than that of silver monomers, in contrast with gallium bombardment. Our results involving ions indicate a similar effect. Their observation was explained by the specific energy dissipation mechanism of fullerene projectiles. Molecular dynamics simulations showed that buckminsterfullerenes create a collective motion of atoms in the silver surface [5,6]. This mesoscale motion induces the formation of a crater in the surface, from which silver atoms and clusters are desorbed. Large clusters with tens of silver atoms may also detach from the rim of the forming crater. In comparison to collision cascade-induced sputtering, the silver atoms desorbed from this superheated nanovolume have a limited amount of kinetic energy, similar to our measurements. It should also be noted that, in knock-on processes, the energy imparted to a silver atom by a carbon atom of the fullerene cannot be more than a fraction of the C atom energy, 250 eV, which is much lower than the energy of the Ga^+ projectile (15 keV).

To our knowledge, it is the first time that the KEDs of molecular and fragment ions sputtered by C_{60}^+ projectiles are reported. The broader distributions observed for the fragment ions and for the Ag-cationized polystyrene tetramers are also resulting from the specific processes induced by fullerene projectiles. We speculate that the collective motion and catapult-like ejection mechanism described in the simulations [5,6] might explain these distributions. It has been observed in previous works that the cooperative uplifting of polystyrene tetramers by several silver atoms gave rise to molecules with a higher kinetic energy than the interaction with a single substrate atom [12]. The collective motion observed under fullerene bombardment appears as an extreme case of cooperative uplifting where virtually all the silver atoms underneath a PS molecule might be moving upward in a concerted manner. Recent MD results involving the desorption of PS tetramers from a silver substrate by fullerene projectiles confirm that, on average, larger translational energies of the ejected molecules are attained [13]. On the other hand, the slightly lower degree of unimolecular dissociation induced by fullerene in comparison with gallium ions is a sign that the internal energies of the ejected fragment ions might be somewhat lower.

In conclusion, the kinetic energy distributions of silver atoms, silver clusters and organic ions sputtered from an overlayer of polystyrene on silver fit and complement the emerging picture of kiloelectronvolt fullerene–solid interaction. The comparatively low energies of silver atoms and large energies of molecular ions might be a natural consequence of the specific type of mesoscale motion induced by buckminsterfullerenes, as described by recent molecular dynamics simulations. At this stage, it is not possible to tell whether the ionization process has any influence on the energy dependence of the sputtered molecular ions. This first report on the energy of molecular ions constitutes new material for fundamental studies of the interaction between fullerenes and thin organic layers. Our future works will also focus on elucidating the desorption processes induced by C_{60}^+ in bulk organic solids, i.e. the type of sample for which the largest yield increases are reported, and on the investigation of the ionization mechanisms at play upon fullerene projectile bombardment.

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