

Secondary Ion Yields Produced by keV Atomic and Polyatomic Ion Impacts on a Self-assembled Monolayer Surface

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A suite of keV polyatomic or 'cluster' projectiles was used to bombard unoxidized and oxidized self-assembled monolayer surfaces. Negative secondary ion yields, collected at the limit of single ion impacts, were measured and compared for both molecular and fragment ions. In contrast to targets that are orders of magnitude thicker than the penetration range of the primary ions, secondary ion yields from polyatomic projectile impacts on self-assembled monolayers show little to no enhancement when compared with monatomic projectiles at the same velocity. This unusual trend is most likely due to the structural arrangement and bonding characteristics of the monolayer molecules with the Au(111). Copyright © 1999 John Wiley & Sons, Ltd.

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The structural and chemical properties of self-assembled monolayers (SAMs) have been studied using a variety of analytical methods.^{1–18} Alkanethiol-based SAMs form highly organized molecular arrays on surfaces, providing reliable models for the study of adsorption, wetting and electron transfer at organic interfaces.^{9,11,19} Currently, applications for monolayers are being developed in the fields of chemical sensing and molecular-based electronics. Chemical sensitivity may be achieved by incorporating chemically selective functionalities into the monolayer, while potential electronic applications will rely on lithographic patterning techniques.^{20–26}

SAMs provide interesting targets for studying desorption phenomena induced by monatomic and polyatomic projectile impacts. *n*-Alkanethiol monolayers on Au(111) spontaneously form densely packed, two-dimensional surface assemblies. Monolayer formation is believed to arise via a Au(I)–S[–] bond, with stabilization imparted by van der Waals interactions among the individual alkane chains.¹⁸ Straight-chain alkanethiols chemisorbed on Au(111) adopt a ($\sqrt{3} \times \sqrt{3}$)R30° overlayer lattice with the carbon chains tilted 30° from the surface normal, in an all-trans conformation. At saturated coverages, nearest-neighbor distances in the monolayer are 5.0 Å, while the Au(111) atoms are separated by 2.9 Å.^{10,11,19} The thickness and order of the monolayer increase with the length of the chemisorbed molecule and can be selected prior to the experiment.¹⁹ In the case of the *n*-hexadecanethiol (CH₃(CH₂)₁₅SH) monolayer employed in our experiments, the molecule adopts a tilted orientation on Au(111) which leads to a thickness of 21 Å.

Several previous comparative studies of polyatomic and atomic projectiles for chemical analysis using secondary ion mass spectrometry (SIMS) used targets consisting of multiple layers of analyte. These targets could be considered infinitely thick relative to the penetration depth of each projectile in the velocity range of 0.01 to 0.15 keV/u. Each study demonstrated the advantage of using polyatomic or 'cluster' projectiles instead of monatomic projectiles.^{27–43} In particular, the cluster projectiles produce non-linear enhancements in the secondary ion (SI) yield when compared at similar impact velocity.^{29,30,33}

The sputter yields produced by atomic and polyatomic primary ions have also been compared using thin organic targets, such as NH₃ adlayers on a CO/Ni surface⁴⁴ and on Langmuir-Blodgett films.⁴⁵ In these studies, although enhancements in ion signal were observed using cluster projectiles, the enhancement from the thin films was reduced compared to thicker targets. At present, the emerging pattern is that polyatomic projectiles produce enhancements in SI yield, but the extent of the enhancement differs depending on the substrate. The largest enhancements are observed from polymer and organic multi-layer targets.

SIMS, using atomic primary ions, has been used in a number of cases to characterize SAM surfaces.^{25,26,46–50} We report here a comparison of the relative SI yields produced by Cs⁺ and various polyatomic primary projectiles on the same ultra-thin SAM target. The experiments described below were conducted in the event-by-event bombardment and detection mode to measure SI yields at the limit of single ion impacts.

EXPERIMENTAL

The experiments were performed in the event-by-event bombardment and detection mode with a primary ion

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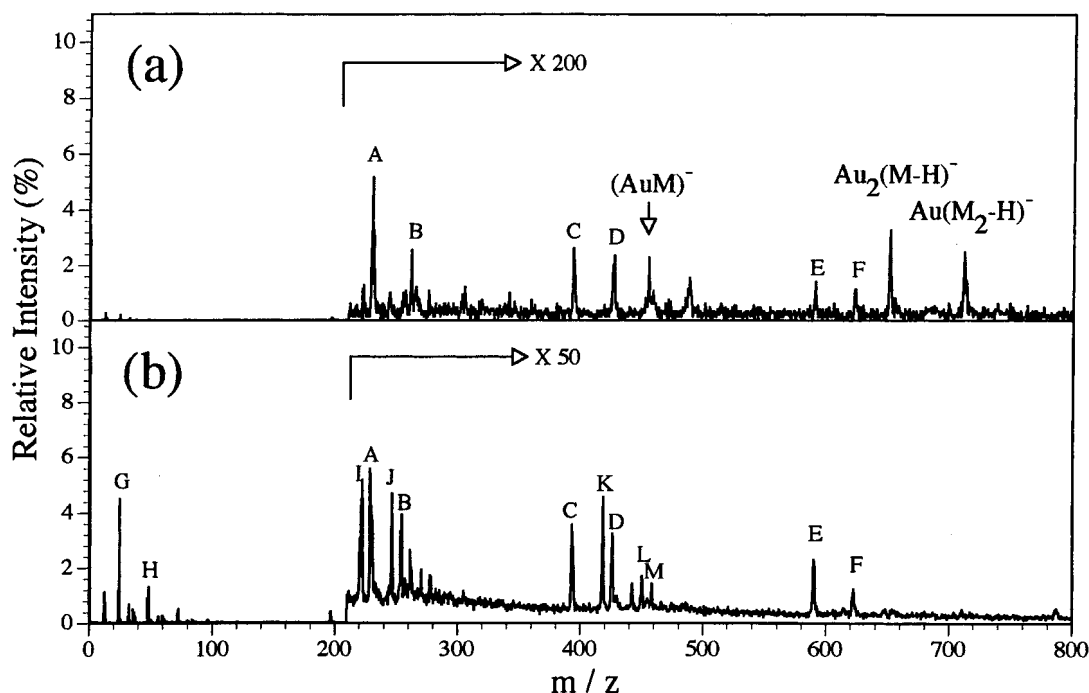


Figure 1. TOF-SI mass spectra of a $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ self-assembled monolayer on Au using (a) Cs^+ and (b) C_{60}^+ projectiles. Both Cs^+ and C_{60}^+ were accelerated to a total energy of 20 keV, resulting in a slower impact velocity for C_{60}^+ . Peak assignment symbols are as follows: A = $(\text{AuS})^-$, B = $(\text{AuSC}_2\text{H})^-$, C = $(\text{Au}_2)^-$, D = $(\text{Au}_2\text{S})^-$, E = $(\text{Au}_3)^-$, F = $(\text{Au}_3\text{S})^-$, G = $(\text{C}_2\text{H})^-$, H = $(\text{C}_4\text{H})^-$, I = $(\text{AuC}_2\text{H})^-$, J = $(\text{AuC}_4\text{H})^-$, K = $(\text{Au}_2\text{C}_2\text{H})^-$, L = $(\text{Au}_2\text{SC}_2\text{H})^-$, M = $(\text{Au}_2\text{S}_2\text{H})^-$.

fluence of ~ 1 – 100 impacts/s. This allowed analysis of SAMs with as few as 10^5 to 10^6 impacts/ cm^2 , virtually eliminating sample alteration and charging during the analysis period. A dual time-of-flight (TOF) SI mass instrument, fully described elsewhere,^{40,41} was used to simultaneously measure sputtered SIs and electrons from a target under keV ion bombardment. Projectiles were created by passing one of a pair of ^{252}Cf fission fragments through an aluminized-mylar foil coated with a thin layer of the primary ion source material. CsI , C_{60} and $\text{Bi}(\text{NO}_3)_3$ (Aldrich) served as parent materials for creating primary ion source foils. The complementary fission fragments started the timing electronics used to measure the flight times of projectiles and secondary ions. Primary projectiles were accelerated and separated in the first TOF field-free region. Secondary electrons were used to signal the impact of a specific projectile on the target surface. The electrons were steered into a microchannel plate (MCP) detector by using a weak magnetic field. SIs were accelerated away from the target, allowed to separate according to their m/z in a second TOF field-free region and then detected at another MCP detector.

A coincidence counting protocol was used to acquire the SI mass spectra. Details of this method have been published in previous work.^{30,35,51–53} Briefly, a time event window was set on the detection of a secondary electron, signaling the impact of a primary ion of interest on the target. All SIs originating from the same start event and detected in coincidence with this electron were stored in a reserved portion of computer memory. By summing events, SI coincidence spectra were produced for a variety of projectiles impacting the same analytical target. Relative SI yields were determined by dividing the integrated peak area of a specific SI in the coincidence spectrum by the

integrated peak area of the secondary electrons within the event window in the electron spectrum (each after appropriate subtraction of background). SI yields were multiplied by 100 and reported as percent (%) relative yield.

The SAMs were adsorbed on Au-coated Si (100) wafers prepared by electron-beam deposition of a 10 nm Ti adhesion layer followed by 200 nm of Au (Lance Goddard Associated, Foster City, CA, USA). The substrates were ozone cleaned (Boekel UV-Clean, Model 135500, Feasterville, PA, USA) for 10 min immediately prior to monolayer deposition. $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ (Aldrich 98%) was purified by a single distillation at reduced pressure. Monolayers were prepared by soaking the substrates in 1.0–1.5 mM ethanolic solution (100% ethanol, Quantum) of the thiol for 18–24 hrs. Immediately prior to analysis, the wafers were removed from the solution, rinsed with ethanol and deionized water (Ultrapure MilliQ water, Millipore, 18 $\text{M}\Omega\text{-cm}$ resistivity), and dried under a stream of N_2 gas. The wafers were then attached to a sample holder using conductive silver paint and shielded from visible light during the drying process (~ 30 min). To produce a thick or multilayer target, an aliquot of the *n*-hexadecanethiol solution in ethanol was pipetted onto a stainless steel sample holder and allowed to dry. The thickness and coverage of the organic film is not known, but is assumed to be thick compared to the thickness of the SAM sample and the range of the primary ions.

RESULTS AND DISCUSSION

Atomic and polyatomic impacts at equal energy

Figures 1 and 2 contain secondary ion mass spectra of a *n*-hexadecanethiol monolayer on Au. The spectra were obtained by bombarding the same monolayer target with

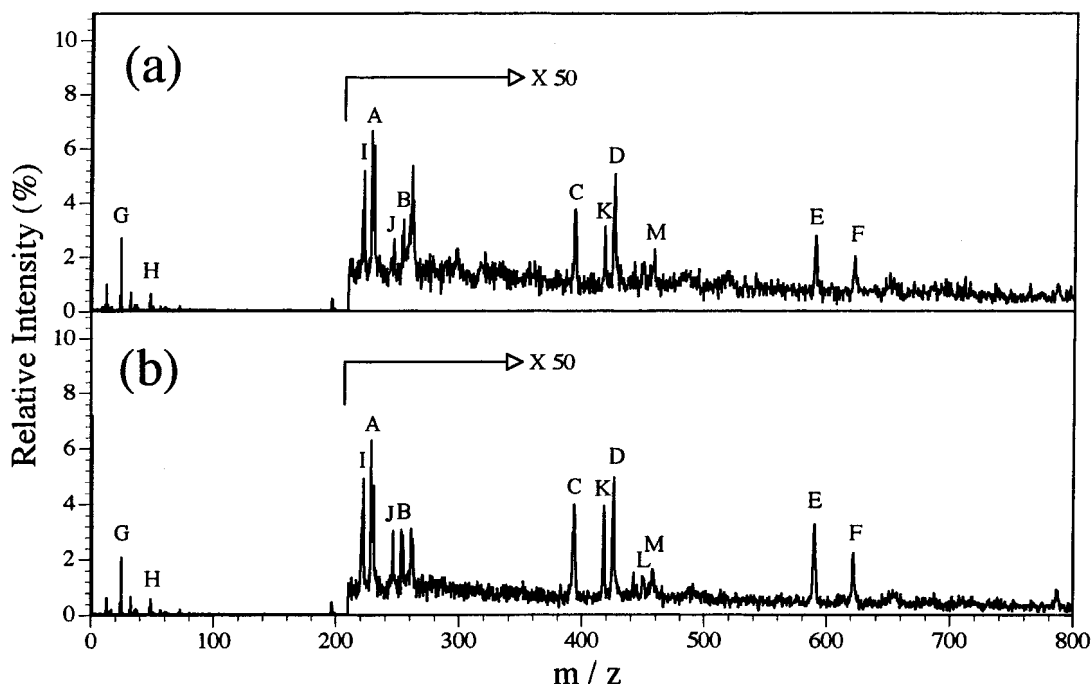


Figure 2. TOF-SI mass spectra of the same $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ self-assembled monolayer on Au using (a) $(\text{Bi}_2\text{O}_3)_3\text{BiO}^+$ and (b) $(\text{Bi}_2\text{O}_3)_2\text{BiO}^+$ projectiles. Both $(\text{Bi}_2\text{O}_3)_3\text{BiO}^+$ and $(\text{Bi}_2\text{O}_3)_2\text{BiO}^+$ were accelerated to a total energy of 20 keV. See caption to Fig. 1 for peak assignment symbols.

20 keV Cs^+ (1a), C_{60}^+ (1b), $(\text{Bi}_2\text{O}_3)_3\text{BiO}^+$ (2a) and $(\text{Bi}_2\text{O}_3)_2\text{BiO}^+$ (2b) projectiles. The peak assignment codes for the spectra in Figs 1 and 2 are listed in the respective figure captions. The mass spectrum in Fig. 1(a) was acquired using $\sim 300\,000$ Cs^+ projectiles, which translates into a total primary ion fluence ca. seven orders of magnitude lower than typical fluences for static SIMS conditions.⁵⁴ None of the four projectiles produced a deprotonated molecular ion, $\text{CH}_3(\text{CH}_2)_{15}\text{S}^-$, at m/z 257. Low molecular ion yields from alkanethiol monolayers on Au have been reported in previous studies.¹⁵ In the spectrum produced by Cs^+ projectiles (1a), secondary ions incorporating Au atoms and the parent molecule (referred to hereafter as Au-molecule ions), however, are present in relatively large abundances. $\text{Au}_2(\text{M} - \text{H})^-$ at m/z 651, where M is the complete alkanethiol molecule, is the most abundant of these Au-molecule ions. Other Au-molecule ions present in high abundances are $\text{Au}(\text{M}_2 - \text{H})^-$ at m/z 712 and AuM^- at m/z 455. The absence of $\text{CH}_3(\text{CH}_2)_{15}\text{S}^-$ molecular ions, as well as the presence of Au-molecule ion clusters, are thought to result from the extremely stable Au-S bonds that are characteristic of this SAM.¹⁵ Other prominent secondary ions in the spectrum include Au_x^- cluster ions and Au_xS_y^- fragment ions.

The spectrum in Fig. 1(b) was acquired using $\sim 500\,000$ C_{60}^+ projectiles. In general, the relative intensities of the secondary ions, including low mass (<100 u) fragment ions, are larger by a factor of four when using C_{60}^+ instead of Cs^+ as the primary ion. An important consideration, however, is that unlike Cs^+ projectiles, 20 keV C_{60}^+ projectiles do not produce the Au-molecule ion clusters at m/z 455, 651 and 712. The C_{60} primary ions do, however, generate secondary ion peaks which are not produced by Cs^+ . These secondary ions, of the form $\text{Au}_x(\text{C}_y\text{H}_z)^-$, most likely originate from fast recombination/rearrangement reactions which transpire on or just above the sample surface. Reactions of this type

have been documented in other studies involving polyatomic projectile impacts.^{15,41,43,55,56} The structure of the SAM contains a framework of C-C and C-H bonds, as well as the Au-thiolate bond. Since Au-C bonds are not present in the original structure of the monolayer, $\text{Au}_x(\text{C}_y\text{H}_z)^-$ ions are most likely an artifact resulting from chemical reactions generated by the polyatomic projectile impacts. It is interesting to note that $\text{Au}_2\text{C}_2\text{H}^-$ is one of the most abundant secondary ions in Fig. 1(b), but is not present in the spectrum produced by Cs^+ impacts.

Figure 2 was acquired using $\sim 130\,000$ $(\text{Bi}_2\text{O}_3)_3\text{BiO}^+$ (2a) and $\sim 180\,000$ $(\text{Bi}_2\text{O}_3)_2\text{BiO}^+$ (2b) projectiles. There is little difference in the mass spectra produced by the $(\text{Bi}_2\text{O}_3)_3\text{BiO}^+$ and $(\text{Bi}_2\text{O}_3)_2\text{BiO}^+$ projectiles, and the spectra in Fig. 2 are very similar to the spectrum in Fig. 1(b) generated by C_{60}^+ projectiles. $(\text{Bi}_2\text{O}_3)_m\text{BiO}^+$ projectiles do not produce Au-molecule ions, but they do produce Au_xS_y^- fragment ions and $\text{Au}_x(\text{C}_y\text{H})^-$ artifact ions similar to SIs from C_{60}^+ impacts.

Cs^+ and $(\text{CsI})\text{Cs}^+$ impacts at equal velocity

Previous work has demonstrated that polyatomic projectiles produce 1–2 orders of magnitude higher molecule ion yields than atomic projectiles when compared at the same energy, even though their velocities are typically lower (velocity is proportional to the kinetic energy per mass unit).^{40,41,43} As illustrated above, however, polyatomic projectile impacts on a SAM surface do not produce Au-molecule ion clusters from the SAM, while monatomic Cs^+ projectiles produce an abundance of Au-molecule ions. A possible explanation for these unusual data involves the thickness of the monolayer and different penetration depths of each projectile resulting from different impact velocities achieved at 20 keV. The more massive C_{60}^+ projectile, for example, is accelerated to an impact velocity of 0.028 keV/u, whereas the smaller Cs^+

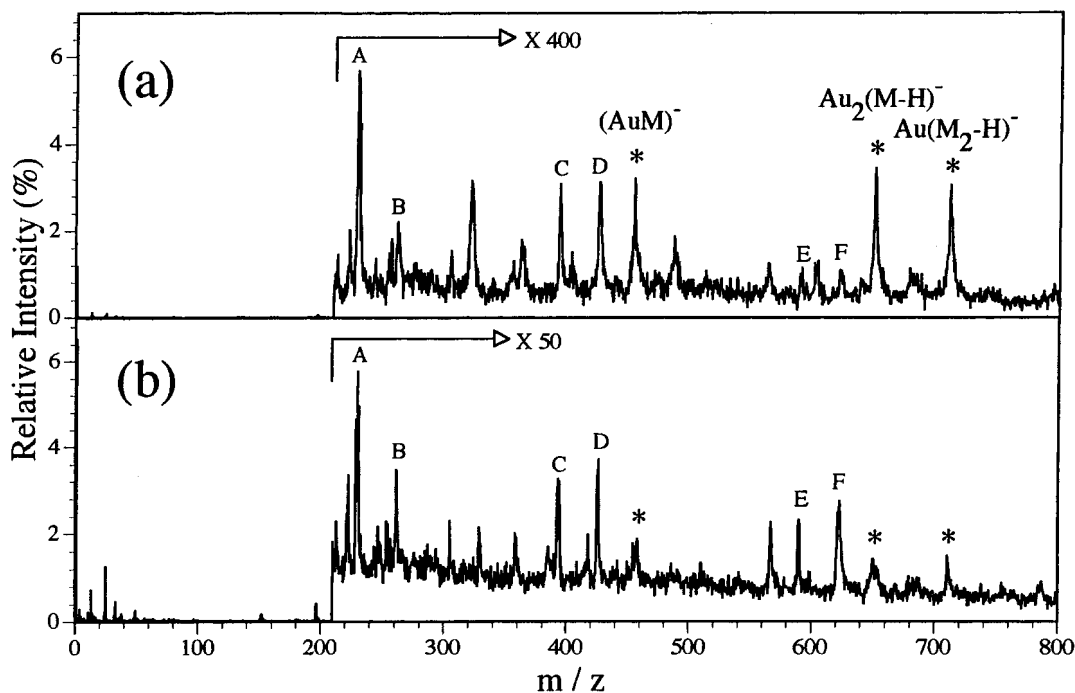


Figure 3. TOF-SI mass spectra of a self-assembled monolayer on Au using (a) 11 keV Cs^+ and (b) 32.5 keV $(\text{CsI})\text{Cs}^+$ impacts. The incident energy per mass unit for the two projectiles is ~ 0.083 keV, resulting in a similar impact velocity. See caption to Fig. 1 for peak assignment symbols.

monatomic projectile achieves a velocity ~ 5 times faster (0.15 keV/u). As a result, the polyatomic projectiles may not achieve sufficient velocity at 20 keV to penetrate through the thickness (21 Å) of the monolayer to deposit energy into the Au substrate in the form of collision cascades. It is thought that these collision cascades within the Au substrate are necessary to desorb intact Au-molecule ions some distance away from the point of projectile impact (with the caveat that carbon atoms in the C_{60} cluster may also be backscattered by collisions with the more massive Au atoms).

To test this hypothesis, Cs^+ and $(\text{CsI})\text{Cs}^+$ projectiles were accelerated to the same velocity and the corresponding Au-molecule ion yields were compared from impacts on the same monolayer target. Figure 3 illustrates the TOF-SI mass spectra of the hexadecanethiol monolayer on Au(111) produced by Cs^+ and $(\text{CsI})\text{Cs}^+$ projectile impacts. The Cs^+ projectiles were accelerated to an energy of 11 keV while the $(\text{CsI})\text{Cs}^+$ projectiles were accelerated to 32.5 keV, giving a similar impact velocity of 0.083 keV/u for each projectile. As shown in Fig. 3(b), Au-molecule ions from $(\text{CsI})\text{Cs}^+$ impacts are now present in low relative abundances. Thus, Au-molecule ions are desorbed by polyatomic projectile impacts on the $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ monolayer if the projectile is given sufficient velocity to penetrate through the thickness of the monolayer and deposit energy into the Au substrate. Due to a limit of ~ 32 kV for ion acceleration in our instrument, we could not compare Cs^+ and cluster projectiles such as C_{60}^+ at a similar impact velocity. Ion acceleration voltages >60 kV are necessary to compare sputtering by C_{60}^+ to Cs^+ at the same impact velocity.

Impacts on UV-oxidized monolayers

UV exposure of alkanethiol monolayers in air results in the oxidation of the thiolate molecules (RS^-) to their corre-

sponding sulfonates (RSO_3^-).^{25,26} For these experiments, SAMs were irradiated with UV light from a Hg lamp for 30 min. Figure 4 is a TOF SI mass spectrum of an oxidized $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ monolayer on Au using $\sim 500\,000$ C_{60}^+ projectiles at 20 keV. Again the deprotonated molecular ion, $\text{CH}_3(\text{CH}_2)_{15}\text{S}^-$, is not present using an impact energy of 20 keV; however, the oxidized molecular ion, $\text{CH}_3(\text{CH}_2)_{15}\text{SO}_3^-$, is present in a high abundance. This suggests that the weaker Au-alkylsulfonate bond leads to a higher sputter yield. The lack of stability would also explain the absence of Au-SO_x and $\text{Au-C}_n\text{SO}_x$ ions in the spectrum. The high yield of $\text{CH}_3(\text{CH}_2)_{15}\text{SO}_3^-$ relative to the thiolate species may also be attributed to a high electron affinity for the former. Electron attachment has been identified as the probable ion formation mechanism in direct laser desorption

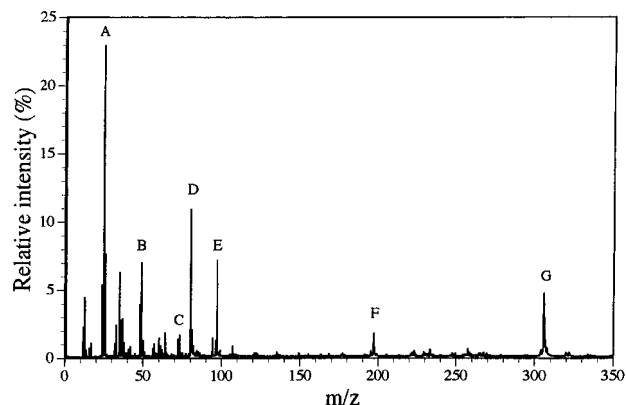


Figure 4. TOF-SI mass spectrum of a $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ self-assembled monolayer on Au after exposure to UV light. The spectrum was produced using C_{60}^+ projectile impacts at 20 keV. Peak assignment symbols are as follows: A = $(\text{C}_2\text{H})^-$, B = $(\text{C}_4\text{H})^-$, C = $(\text{C}_6\text{H})^-$, D = SO_3^- , E = HSO_4^- , F = Au^- , G = $[\text{CH}_3(\text{CH}_2)_{15}\text{SO}_3]^-$.

Table 1. Relative secondary ion (SI) yield ratios from projectile impacts on the same monolayer surface. The ratios are expressed as the yield of a specific (SI) from a polyatomic primary ion divided by the yield of the same (SI) produced by Cs⁺ projectiles

Primary ion ↓	(C ₂ H) [−]	(C ₄ H) [−]	SO ₃ [−]	HSO ₄ [−]	Au [−]	CH ₃ (CH ₂) ₁₅ SO ₃ [−]
Cs ⁺	1	1	1	1	1	1
C ₆₀ ⁺	14	36	4.1	3.2	2.5	2.1
(Bi ₂ O ₃)BiO ⁺	3.5	4.9	3.3	3.6	2.1	2.2
(Bi ₂ O ₃) ₂ BiO ⁺	5.6	12	4.7	4.1	3.6	2.6

of monolayer surfaces.¹⁶ If the difference in the yield of molecule ions from the unoxidized and oxidized surfaces in SIMS is assumed to be due to changes in ionization probability, our results differ from direct laser desorption/Fourier transform mass spectrometric studies of unoxidized and oxidized alkanethiol monolayers by Scott *et al.*⁵⁷ in which the thiolate and sulfonate species were found to have the same ionization probabilities.

The spectrum in Fig. 4 suggests that complete penetration by the projectile through the monolayer to deposit energy directly into the gold substrate is not necessary to produce high yields of oxidized molecular ions. Collisions induced by the polyatomic projectile within the monolayer may lead to the ejection of oxidized molecular ions. We cannot rule out, however, that portions of the SAM were photooxidized and photodesorbed during UV exposure, leading to defects in the monolayer (i.e. holes, pits, etc.) that would permit direct access of the primary ion to the Au surface.

The same oxidized monolayer was also analyzed with 20 keV Cs⁺, (Bi₂O₃)BiO⁺ and (Bi₂O₃)₂BiO⁺ projectiles. Table 1 lists the yield improvement produced by each polyatomic projectile. The yield improvements were calculated by dividing the yield of a particular SI produced by a polyatomic ion by the yield of the same SI generated by Cs⁺ projectiles. When compared at the same incident energy, cluster projectiles give ~2 times more of the oxidized molecular ion than Cs⁺ projectiles. The cluster projectiles, however, produce even more SO₃[−], HSO₄[−] and C_xH[−] fragment ions when compared with Cs⁺ projectiles. In particular, C₆₀⁺ projectiles produce an abundance of C_xH[−] fragment ions most likely due to recombination/rearrangement processes. Although recoiled projectile atoms have been previously reported in SI spectra, it is unlikely that C_xH[−] ions originate from the recoil of carbon atoms within C₆₀⁺.^{58–60} This process would require carbon atoms within the C₆₀⁺ projectile to acquire a hydrogen atom from the sample surface before recoiling. Also, other cluster projectiles which do not contain carbon atoms produce a similar increase in the formation of C_xH[−] SIs. Therefore, the carbon cluster SIs most likely represent 'damaged' monolayer molecules, resulting from induced chemistry near a polyatomic projectile impact.

SI yield enhancement

Cs⁺ and (CsI)Cs⁺ projectiles were also compared at an equal velocity (0.083 keV/u) on the UV-oxidized monolayer and on a thick multilayer deposit of CH₃(CH₂)₁₅SH on a stainless steel substrate. Table 2 allows determination of the SI yield enhancement (the yield increase *per atom* in the projectile), since the primary ions are compared at an equal velocity. In the event of a linear ion yield increase, the yield of SIs from (CsI)Cs⁺ projectiles (YSI(CsI)Cs⁺) should be three times the yield from Cs⁺ projectiles (YSI(Cs)⁺). Since (CsI)Cs⁺ has three similar mass constituents, the yield enhancement compared with Cs⁺ projectiles is obtained by dividing the SI yield ratio (YSI(CsI)Cs⁺/YSI(Cs)⁺) by three (the number of constituents in the polyatomic projectile). A yield enhancement >1 is considered supralinear and the cluster projectile produces more SIs than impacts of three separate monatomic projectiles. Yield enhancements <1 are sublinear and atomic ion projectile impacts produce more SIs, *per incoming atom*, than a cluster projectile.

Table 2 shows the yield enhancements for the Au-molecule ions and the oxidized molecular ion produced by (CsI)Cs⁺ impact on the three targets examined. At 32.5 keV impact energy, the yield of (AuM₂−H)[−] per projectile constituent produced by (CsI)Cs⁺ is 0.6 of that produced by 11 keV Cs⁺ projectiles. The enhancement in CH₃(CH₂)₁₅SO₃[−] yield from (CsI)Cs⁺ impacts on the oxidized monolayer is 1.4, which is much less than the yield enhancement of 7.4 observed for (CsI)Cs⁺ impacts on the the alkanethiol coating on stainless steel.

Comparative measurements of ion yields and yield enhancements following atomic and small polyatomic projectile impacts on thin organic films have recently been reported. For instance, Hanley and co-worker studied the sputtering of an ultra-high vacuum prepared thin-film surface by low energy (<1 keV) Xe⁺ and SF₅⁺.⁴⁴ In their study, the target surface was composed of a NH₃ layer physisorbed to a CO layer chemisorbed to a Ni surface. At the low incidence energies employed, where direct knock-on sputtering predominates, an enhancement in the yield of NH₃ by the SF₅ primary ion was attributed to the reflection of the projectile atoms by the Ni surface. In our experiments, sputtering by the 20 keV atomic and polyatomic projectiles is predominantly via the generation of collision cascades within the Au substrate, and the reflection of projectile components is not likely. In a more recent study, Stapel *et al.* demonstrated that the yield enhancement produced by SF₅⁺ projectiles (over Ar⁺ and Xe⁺ projectiles at equal impact energy) on a single Langmuir-Blodgett layer is significantly lower when compared to multilayers.⁴⁵ The results of our study demonstrate that, within our experimental error, there is no net enhancement for alkane thiolate and a small enhancement for alkane sulfonate molecules sputtered from self-assembled monolayers on Au by 20 keV (CsI)Cs⁺. Recent molecular dynamics simulations by

Table 2. Secondary ion yields and yield enhancements produced by Cs⁺ and (CsI)Cs⁺ projectile impacts at the same energy per mass unit. The targets used were: (a) a CH₃(CH₂)₁₅SH monolayer on Au, an oxidized CH₃(CH₂)₁₅SH monolayer on Au and a multilayer (see text) of CH₃(CH₂)₁₅SH on stainless steel

Target	Secondary ion	Cs ⁺ 11 keV	(CsI)Cs ⁺ 32.5 keV	$\frac{YSI(CsI)Cs}{YSI(Cs)}$	Yield enhancement
Monolayer	(AuM ₂ −H) [−]	0.052	0.10	1.9	0.6
Oxidized monolayer	CH ₃ (CH ₂) ₁₅ SO ₃ [−]	0.21	0.90	4.3	1.4
Multilayer target on stainless steel	CH ₃ (CH ₂) ₁₅ SH [−]	0.085	1.9	22	7.4

Krantzman and co-workers,⁶¹ using Cu_n projectile impacts on a monolayer of biphenyl molecules on a Cu surface, failed to predict yield enhancements from polyatomic ion bombardment, though the yield to damage ratio was predicted to increase.

The individual collision cascades generated by the constituents in a polyatomic projectile overlap in space and time. This, in turn, increases the energy density deposited into the surface and near surface region of a solid. According to the existing model of polyatomic ion impacts, ion yield enhancements are attributed to the adjacent collision cascades collaborating, producing multiple 'hits' on a surface molecule and increasing the ejection probability. Since the molecules in a SAM are attached to the surface by a single Au–S bond, and stand 'on end' (but slightly tilted with respect to the surface normal) with respect to the Au substrate, it is unlikely that two or more cascades will overlap in this small area at the same time. The sputtering of a thiolate or sulfonate molecule from the Au surface will likely be due to the intersection of a single cascade with the Au/monolayer interface and, as such, efficiency in sputtering by (CsI)Cs⁺ over Cs⁺ in the energy range used in this study is expected to scale linearly with the number of projectile atoms. This ordered arrangement of the monolayer/Au system is different from the organic multilayer targets used in previous studies. In thicker targets, a polyatomic projectile will generate collision cascades within the organic material, and the probability that multiple cascades will intersect cooperatively to eject a surface molecule is higher.

CONCLUSIONS

Relative secondary ion yields from keV energy atomic and polyatomic projectile impacts on the same SAM surface were measured and compared. Ion emission from monolayer systems allows the evaluation of cluster projectile performance on targets where the amount of analyte is limited to that of a single, two-dimensional monolayer. The organic molecules that comprise SAMs are attached to the Au substrate by a single, specific Au–S bond which is thought to be covalent in nature and extremely stable. This situation is different from, for instance, the physisorption of organic molecules to a surface or the van der Waals type forces in a molecular solid. One would expect to see some SI yield enhancement on surfaces with monolayer or submonolayer coverage, as long as the molecular orientation allows collision cascades from projectile impacts to overlap in space and time at the same molecule. A slight yield enhancement for intact molecule ions sputtered from the monolayer is observed for polyatomic ion impacts. The enhancement is smaller, however, than those that are observed from thicker targets used in this study and in previous experiments.^{29,33}

Acknowledgements

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