
Chemical Modification of Fluorinated Self-Assembled Monolayer Surfaces by Low Energy Reactive Ion Bombardment

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Reactive collisions of low energy (< 100-eV) mass-selected ions are used to chemically modify fluorinated self-assembled monolayer surfaces comprised of alkanethiolate chains $\text{CF}_3(\text{CF}_2)_{11}(\text{CH}_2)_2\text{S}$ — bound to Au. Typical experiments were done by using 1-nA/cm² beams and submonolayer doses of reactant ions. Characterization of the modified surface was achieved by in situ chemical sputtering (60-eV Xe^{++}) and by independent high mass resolution time-of-flight-secondary ionization mass spectrometry (TOF-SIMS) (15–25-keV, Ga^+) experiments. Treatment with $\text{Si}^{35}\text{Cl}_4^+$ produced a surface from which Xe^{++} sputtering liberated $\text{CF}_2^{35}\text{Cl}^+$ ions, which suggested Cl-for-F halogen exchange at the surface. Isotopic labeling studies that used $\text{Si}^{35}\text{Cl}_2^{37}\text{Cl}_2^+$, and experiments with bromine-containing and iodine-containing projectiles, confirmed this reaction. High mass resolution TOF-SIMS spectra, as well as high spatial resolution images, provided further evidence as to the existence of halogen-exchanged species at the bombarded surface. Analogous Cl-for-F halogen substitution was observed in a model gas-phase reaction. The ion-surface reaction is suggested to proceed through an intermediate fluoronium ion in which the projectile is bonded to the target molecule. The most significant conclusion of the study is that selective chemical modification of monolayer surfaces can be achieved by using reactive ion beams, which lead to new covalent bonds at the surface and in the scattered ions. (*J Am Soc Mass Spectrom* 1995, 6, 187–194)

Chemical modification of surfaces can be achieved by a number of methods. These methods range from exposure to chemical reagents in solution or the vapor phase to more specific treatments, which include ion beam implantation [1–3], molecular beam scattering [4, 5], and plasma etching [6, 7]. The collisions of atoms, molecules, and ions with surfaces are of particular interest for controlled surface chemical modification. Selection of an appropriate atomic, molecular, or ionic reagent, at the optimum collision energy, should make it possible to achieve selective chemical modification of the outermost atomic monolayers of a surface. If such modifications are made to selected areas of the surface, a form of highly specific chemical writing of high spatial resolution might be developed. In spite of its technological appeal, this

objective has been explored surprisingly little, in part because of the difficulty in creating appropriate beams of neutral reagents in sufficient flux at the necessary energies, and in part because there has been relatively little interest in the topic of low energy collisions of polyatomic organic ions with surfaces. This is in contrast to corresponding studies that involve monoatomic or diatomic ion collisions, a subject recently reviewed by Rabalais and co-workers [8]. Reactive molecular beam scattering has been of interest to Ceyer [9] and others [10] who have studied the changes produced at the surface, in addition to changes in the scattered beam. Jacobs and co-workers [11] and others [12, 13] have performed increasingly elegant studies of ion beam scattering, but the effects on the surface have been a secondary concern.

Ion-surface inelastic collisions are well known as a means of effecting dissociation of mass-selected ions and this procedure, termed surface-induced dissociation (SID), has been implemented on mass spectrometers of several types [14–23]. In the course of these

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studies, reactive collisions often have been observed. Early studies showed that fluorine atoms can be picked up from the surface by ionized metal carbonyls, whereas hydrogen and alkyl group abstraction often was observed by aromatic and other ions [23-26]. Recently, a systematic study of some transition metal projectiles, as well as of a large number of group IIIA to VIIA atomic projectiles, revealed that MF_m^+ ($m = 1-5$) scattered products readily are observed upon collisions of atomic ions at fluorinated self-assembled monolayer (F-SAM) surfaces [27, 28]. By changing the nature of the surface and the scattering conditions, much is being learned about the mechanisms of these reactive scattering processes through study of the reactively scattered ions. The present paper also is concerned with reactive collisions of low energy (< 100 -eV) projectile ions at F-SAM surfaces, but attention is given to characterization of the chemically modified surface, rather than to the scattered ionic product, as was the case in previous work.

Surface modification is an almost inevitable consequence of abstraction of an atom from the surface by a projectile ion because a radical site is generally created. This radical may be stabilized by (1) elimination of an atom or group, which leads to the formation of an unsaturated bond, (2) reaction with an adsorbate molecule, or (3) reaction with an adjacent surface-bound chain to cause chain linking and radical propagation. If dissociation of the projectile occurs at the surface, a neutral fragment from this reaction is another candidate to become attached to the radical site.

Experimental

Fluorinated SAM surfaces $CF_3(CF_2)_{11}(CH_2)_2S-Au$, were provided by C. E. D. Chidsey; details of their preparation and properties are reported elsewhere [29, 30]. The surfaces were rinsed with hexane and air-dried before use. A fresh surface was used in each new experiment. All chemicals were from Aldrich (Milwaukee, WI) and were used as received. The ion-surface reaction experiments were studied in a custom-built, hybrid mass spectrometer of BEEQ geometry (B = magnetic sector, E = electric sector, and Q = quadrupole mass analyzer) [31]. The projectile ions, generated by electron impact (70 eV, 10^{-5} torr sample pressure), were mass and energy selected by using the B and E fields, respectively, and then decelerated to 60-eV laboratory translational energy for collision with the surface in the scattering chamber maintained at or below 10^{-8} torr. The incident angle was fixed at 55° with respect to the surface normal and the scattering angle was 90° with respect to the incident beam direction. The primary ion current density was 1 nA/cm^2 and the spot size was about 3 mm^2 . Typical bombardment times for surface modification ranged from 20 min to 2 h. Assuming 10^{14} ions/ cm^2 as the monolayer coverage, total ion doses of 20-min to 2 h bombardment correspond to 0.1 to 0.5 monolayer de-

position. Scattered ion mass spectra were recorded by scanning the quadrupole mass analyzer, with the secondary ion electrostatic analyzer operated to maximize detected scattered ion current. Chemical sputtering [32, 33] with 60-eV $^{132}\text{Xe}^{+}$ as the projectile ion, was applied to examine the surface composition before and after prolonged reactive ion bombardment. Some surfaces also were examined by high resolution time-of-flight secondary ionization mass spectrometry (TOF-SIMS) via a Charles Evans & Associates TFS series instrument (Redwood City, CA). Both high mass resolution spectra (15 keV, Ga^+) and high spatial resolution images (25 keV, Ga^+) were recorded. The static SIMS limit was not approached in these experiments. The samples were analyzed by TOF-SIMS some 2 days after bombardment in the BEEQ instrument. During this period, they were exposed to air, but the possible effects of this exposure were not studied. However, the F-SAM surfaces themselves have been shown to be unaffected by prolonged exposure to air [30]. Similarities were sought between the reactions that occur in ion-surface reactions and model ion-molecule reactions. For this purpose, a triple quadrupole mass spectrometer, Finnigan-MAT TSQ 700 (San Jose, CA) was used to examine the gas-phase ion-molecule reactions. Mass-selected projectile ions, produced by 70-eV electron impact ionization, were allowed to react with perfluorohexane (1 mtorr) at a nominal 2-eV laboratory collision energy in the second (rf-only) quadrupole. Product ions were recorded by scanning the third quadrupole.

Results and Discussion

Silicon-containing ions, like many other monatomic or polyatomic ions [28], undergo reactive scattering from fluorinated SAM surfaces and fluorine is incorporated into the scattered products. For example, SiCl_n^+ ($n = 0-4$) at laboratory collision energies between 20 and 60 eV yields scattered ions that include products due to (1) chemical sputtering, for example, C_3F_5^+ ; (2) surface-induced dissociation, for example, SiCl^+ , as well as (3) products due to ion-surface reactions, for example, SiF^+ , SiClF^+ , and SiCl_2F^+ (Figure 1). Chemical sputtering products, C_nF_m^+ ($n = 1-3$, $m = 1-5$), are most pronounced at higher collision energies, that is, above 40 eV; however, SID and ion-surface reaction products are generated efficiently even at lower collision energy. The reactively scattered ions SiF^+ , SiClF^+ , and SiCl_2F^+ all contain fluorine derived from the surface. The occurrence of fluorine abstraction suggests that changes in the final chemical state of the surface must occur as a result of ion bombardment.

To investigate the changes that the reactive species have caused to the chemical nature of the surface, the surface itself must be characterized. Chemical sputtering mass spectra allow surface characterization because they reflect processes in which ionized fragments from the surface itself, or from an adsorbate, are

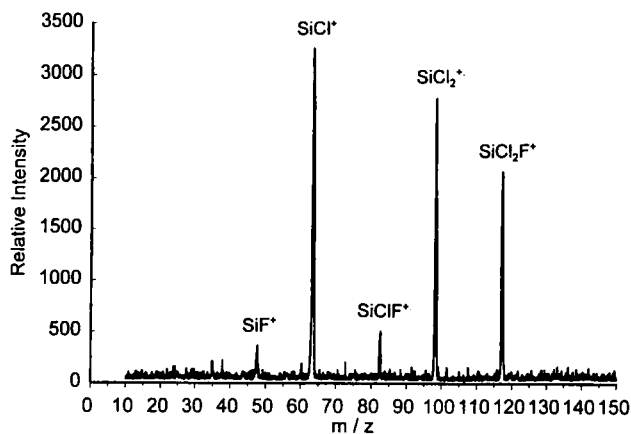


Figure 1. Scattered ion mass spectrum recorded upon 20-eV collision of a $\text{Si}^{35}\text{Cl}_2^+$ projectile at a fluorinated SAM surface. Note the appearance of ion-surface reaction products SiCl_2F^+ , SiClF^+ , and SiF^+ .

ejected following a charge exchange process [32]. Therefore, chemical sputtering spectra were taken before and after prolonged ion bombardment with SiCl_n^+ beams. These spectra were obtained by using 60-eV Xe^{++} projectiles and they displayed changes induced at the surface as a result of prolonged reactive ion bombardment. For example, prior to $\text{Si}^{35}\text{Cl}_4^+$ ion beam bombardment of the surface, no feature at m/z 85 ($\text{CF}_2^{35}\text{Cl}^+$) could be observed in the Xe^{++} chemical sputtering experiment; however, $\text{CF}_2^{35}\text{Cl}^+$ ion was clearly observed after a 2-h surface exposure to a 60-eV $\text{Si}^{35}\text{Cl}_4^+$ ion beam. This result was confirmed by an isotopic study via a $\text{Si}^{35}\text{Cl}_2^{37}\text{Cl}_2^+$ projectile, and again attention was focused on the changes in the pattern of ions observed in the chemical sputtering spectra recorded before and after ion bombardment (Figure 2). Typical 60-eV Xe^{++} chemical sputtering peaks, CF^+ (m/z 31), CF_2^+ (m/z 50), CF_3^+ (m/z 69), C_2F_3^+ (m/z 81), and C_3F_3^+ (m/z 93), were observed in both spectra, with some variation in intensity. Before $\text{Si}^{35}\text{Cl}_2^{37}\text{Cl}_2^+$ bombardment, a low intensity peak, which may be due to an impurity, appeared at m/z 85, whereas no peak at m/z 87 was observed (Figure 2a). After ion beam bombardment, peaks at m/z 85 and 87 in roughly equal abundance were recorded (Figure 2b). This result suggests, although it does not conclusively prove, that the peaks are due to $\text{CF}_2^{35}\text{Cl}^+$ and $\text{CF}_2^{37}\text{Cl}^+$, respectively. The presence of these peaks indicates that the chemical conversion of $-\text{CF}_3$ groups to $-\text{CF}_2\text{Cl}$ groups on the surface might have occurred upon reactive ion beam bombardment.

Static secondary ion mass spectrometry (SSIMS) has been used in characterization of SAM surfaces [34, 35]. Its advantages include high sensitivity, high mass and spatial resolution, and the ability to detect submonolayer quantities of organic materials. High resolution TOF-SIMS spectra via 15-keV Ga^+ ion bombardment further verified the results for the $\text{Si}^{35}\text{Cl}_2^{37}\text{Cl}_2^+$ treated surface; they showed the expected exact masses and

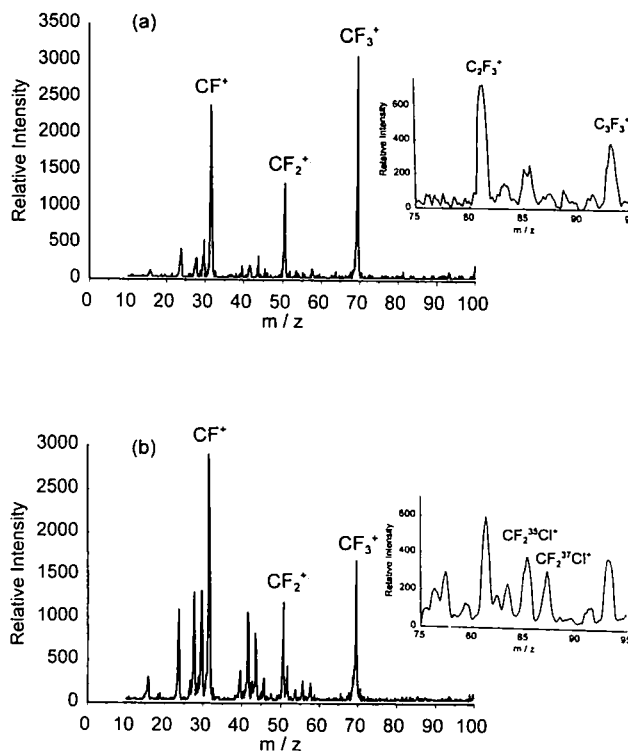


Figure 2. Chemical sputtering spectra recorded upon 60-eV collision of $^{132}\text{Xe}^{++}$ at a fluorinated SAM surface (a) before and (b) after bombardment with 60-eV $\text{Si}^{35}\text{Cl}_2^{37}\text{Cl}_2^+$ projectile for 2 h. Insets show portions of the spectra at high gain. Note the appearance of peaks at m/z 85 and 87 in (b). Peaks at m/z 81 and 93 are due to chemical sputtering (see text).

isotopic abundance ratios (Figure 3). The peaks due to Cl-for-F substitution again appear at the value of m/z 85 and 87. Note the doublet at the nominal value of m/z 81; the low mass peak is due to C_2F_3^+ (sputtering of the SAM surface), whereas the high mass peak originates from the hydrocarbon adsorbate (C_6H_9^+). Low energy ion bombardment of surfaces may create radical sites in situ, which simultaneously or subsequently react with species that are generated by surface collision processes, including ion-surface reactions, SID, and chemical sputtering. The annealing of either ionic, radical, or neutral species to the F-SAM surface reactive sites would alter the chemical composition of the functional groups at the outermost atomic layers. Such chemical changes can be permanent if new covalent bonds (in this case, C—Cl) are formed while old covalent bonds (C—F) are broken. The net result of such bond forming and breaking in this case is halogen exchange. A possible mechanism of halogen exchange is proposed in Scheme I, which illustrates reactions between a F-SAM surface, simplified as RC_2F_5 , and a SiCl_2^+ projectile ion. Upon collision, the unsaturated projectile can form a Si—F—C bond at the terminal $-\text{C}_2\text{F}_5$ group through a positively charged fluoronium ion. Subsequent fluorine transfer from an adjacent C—F bond to the silicon will result in a new Si—F bond and leaves a free radical site at

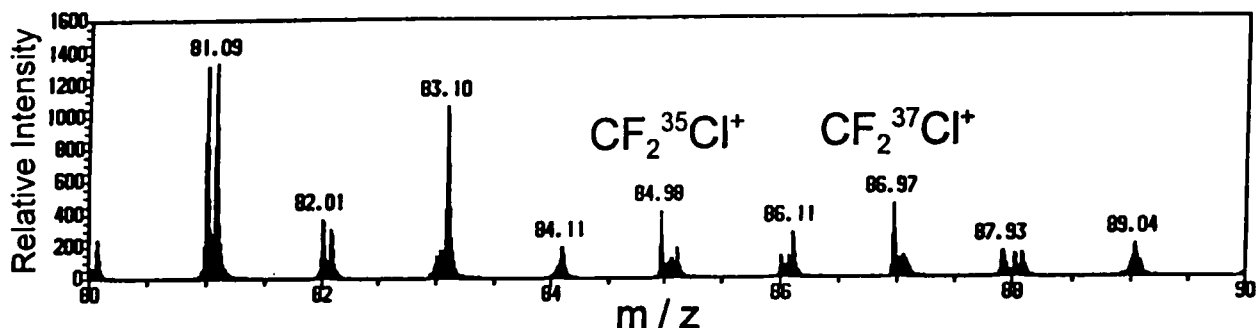
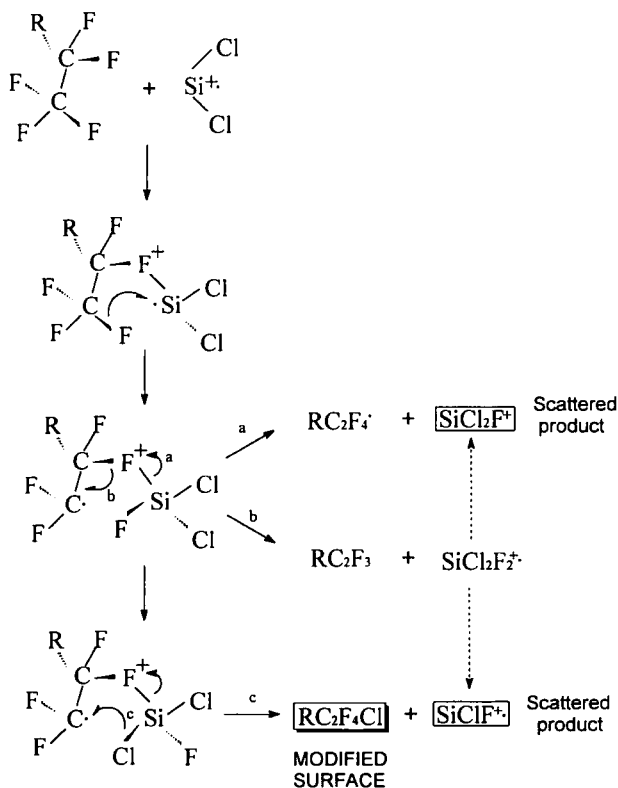


Figure 3. High resolution TOF-SIMS spectrum (15 keV, Ga^+) of a fluorinated SAM surface after bombardment with 60-eV $\text{Si}^{35}\text{Cl}_2^{37}\text{Cl}_2^{+}$ projectile for 2 h. The mass scale calibration was done by selecting peaks of known identity (e.g., CF^+ , CF_3^+ , and C_2F_5^+).

carbon. The intermediate thus formed is composed of two moieties, again bonded together through a fluoronium ion. This intermediate can dissociate to yield either (a) a surface-bound radical and a scattered product ion SiCl_2F^+ or (b) a surface-bound olefin and an unstable gaseous ion $\text{SiCl}_2\text{F}_2^+$, which may fragment to give observed scattered products SiClF^+ and SiCl_2F^+ . The fluoronium intermediate may also rearrange to form a C—Cl bond that leads to (c) the formation of SiClF^+ and the Cl-for-F modified surface. The observation of the chemical sputtering product CF_2Cl^+ indicates that the chlorine is most likely bonded to the outermost carbon of the fluoroalkyl chain.



Scheme I. Possible mechanism for halogen exchange between SiCl_2^+ and a fluorinated SAM surface (RC_2F_5).

There are a number of additional mechanistic issues that need attention. The illustrated mechanism implies that the fluoronium ion in the reactive intermediate binds at the second carbon of the fluoroalkyl chain, whereas the free radical site is at the terminal carbon. This allows the chlorine of the projectile to attach to this carbon without further halogen exchange or rearrangement. It is also possible that the fluoronium ion is initially generated at the terminal carbon, which creates a radical site at the adjacent carbon atom. In this case, chlorine from the projectile is most probably bonded to the second carbon before it undergoes rearrangement and halogen exchange to yield CF_2Cl^+ ions. Although the foregoing mechanistic suggestions are consistent with the experimental results, it is not claimed that alternative possibilities can be excluded. However, projectile penetration more deeply into the SAM structure at the collision energies employed seems highly unlikely; even at 500-eV Xe^{++} energy, the sampling was suggested to be limited to the uppermost portion of the SAM chains [35]. Another possibility is that instead of involving two carbons on the same chain, the silicon species may bridge across two adjacent fluoroalkyl chains. After the elimination of the Cl—Si—F⁺ moiety, a C—C single bond might then form between the two chains. The cleavage of C—F and C—Cl bonds, with concomitant formation of a C—C bond, is energetically more favorable than the formation of one C=C double bond between two carbons of the same chain. However, this linkage would significantly distort the orientation of both chains, because the spacing between unlinked chains in this type of F-SAM is around 6 Å [36] whereas the C—C bond length is about 1.5 Å. This cross chain C—C bond formation does not lead to the proposed halogen exchange at the surface, but it might be a competitive process that affects the outcome of surface modification.

The proposed mechanism accounts for all experimental observations; nevertheless, more direct evidence is needed to confirm that it does take place and that a covalent C—Cl bond has indeed been formed.

We are currently investigating the probability of obtaining such information through techniques like electron energy loss spectroscopy. On the other hand, some alternative mechanisms can be ruled out based on the experimental evidence already available. For example, the possibility that SiCl_4^+ projectiles decompose at the surface to form Cl and Si atoms and that upon sputtering with Xe^+ , CF_2^+ and Cl species recombine in the gas phase to produce CF_2Cl^+ does not seem likely because CF_2^+ and CF_3^+ are much more abundant as sputtered surface fragments, and yet their products with Cl atoms are not observed. Also, if Si were adsorbed at the surface, there should be some Si^{++} or SiF^+ observed in the products [28]; none has been found in either Xe^{++} sputtering or TOF-SIMS experiments. Similar arguments could be put forward against a mechanism that involves adsorption of SiCl_4^+ or other silicon-containing species at the surface.

Surface bombardment with ions that contain halogens other than chlorine was performed in an attempt to generalize the reaction. In an experiment in which the fluorinated surface was bombarded with $\text{CH}_2^{79}\text{Br}^+$ and C^{81}Br^+ projectile ions (mass selected from CH_2Br_2 as a doublet at m/z 93) for 2 h, a new peak at m/z 129, which represents $^{79}\text{BrCF}_2^+$, appeared in the subsequent 60-eV Xe^{++} chemical sputtering spectrum (Figure 4). Although the peak at m/z 131 is largely due to C_3F_5^+ , a product of chemical sputtering of the surface, there is also a small contribution to the peak from $^{81}\text{BrCF}_2^+$ species. This is consistent with the fact that m/z 93 projectile ions consist of 90% $\text{CH}_2^{79}\text{Br}^+$ and 10% C^{81}Br^+ , as judged from the 70-eV electron impact mass spectrum of CH_2Br_2 . In another experiment, a copper grid (50 mesh, 0.01-in wire diameter) was placed in front of the surface during the 2-h bombardment. TOF-SIMS images for the $\text{CH}_2^{79}\text{Br}^+$ bombarded surface showed that bromine was higher in intensity in exposed areas than in covered areas; by contrast, the intensity of fluorocarbon species, such as CF_3^- , was lower in exposed areas (Figure 5). When $\text{CH}_2^{81}\text{Br}^+$ (m/z 95) was used as the projectile ion under identical conditions, the peak at m/z 129 ($^{79}\text{BrCF}_2^+$) disappeared, as expected, whereas the peak at m/z 131 increased noticeably in abundance. Analogous experiments that used CH_2I_2^+ as the projectile gave the corresponding product CF_2I^+ , the presence of which also was confirmed by high resolution TOF-SIMS. The foregoing studies provide further support for the conclusion that the outermost portion of a fluorinated self-assembled monolayer surface can be modified to yield $-\text{CF}_2\text{X}$ groups by reactive ion bombardment.

The chemical nature of the projectile, as well as the surface exposure time, also affects the outcome of surface modification experiments. For example, by using $\text{P}^{35}\text{Cl}_3^+$ as the projectile, the sputtering product diagnostic of Cl-for-F halogen exchange namely, CF_2Cl^+ (m/z 85), was observed after 20-min bombardment (Figure 6). Although the peak at m/z 85 also could be due to PClF^+ , the fact that no peak that

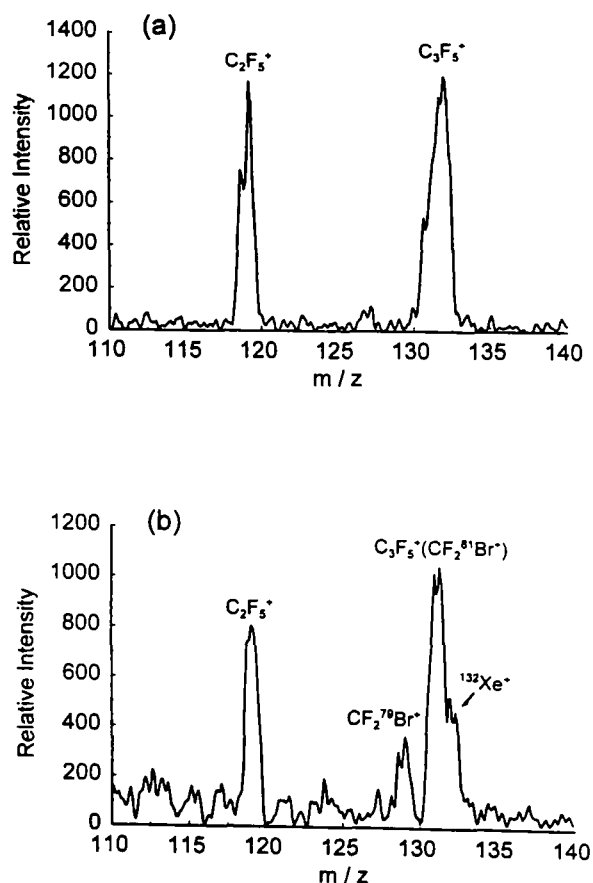


Figure 4. Partial chemical sputtering spectra recorded upon 60-eV collision of $^{132}\text{Xe}^+$ at a fluorinated SAM surface (a) before and (b) after bombardment with 60-eV $\text{CH}_2^{79}\text{Br}^+$ (mass selected m/z 93 from CH_2Br_2) for 2 h. Note the appearance of the peak at m/z 129 in (b). Alternative species given in parentheses are discussed in the text.

corresponds to the fragment PCl^{++} was observable at m/z 66 in the chemical sputtering spectra indicates that it is highly unlikely that m/z 85 represents PClF^+ . To achieve a similar result in Cl-for-F exchange, it took 2 h of bombardment with a SiCl_4^+ projectile (Figure 2b), but only 20 min with a PCl_3^+ projectile (Figure 6b). With a $\text{C}^{79}\text{Br}_3^+$ projectile, 20-min bombardment showed no evidence of significant Br-for-F halogen exchange, but after 2 h, the expected product CF_2Br^+ was observed. Ion beam dose dependence indicates the rate differences for various surface processes that are involved in modification.

A study that used P^{35}Cl^+ projectile ions at 60-eV collision energy showed PF^+ and PClF^+ as scattered ion-surface reaction products (Figure 7). Chemical sputtering peaks are also intense in this spectrum. It is difficult to determine the relative contribution of phosphorous and CF to these peaks because they both have the mass of 31 u. However, based on previous results, formulas in parentheses in the figure represent the probable compositions of the minor components. The occurrence of extensive fluorine abstraction from the

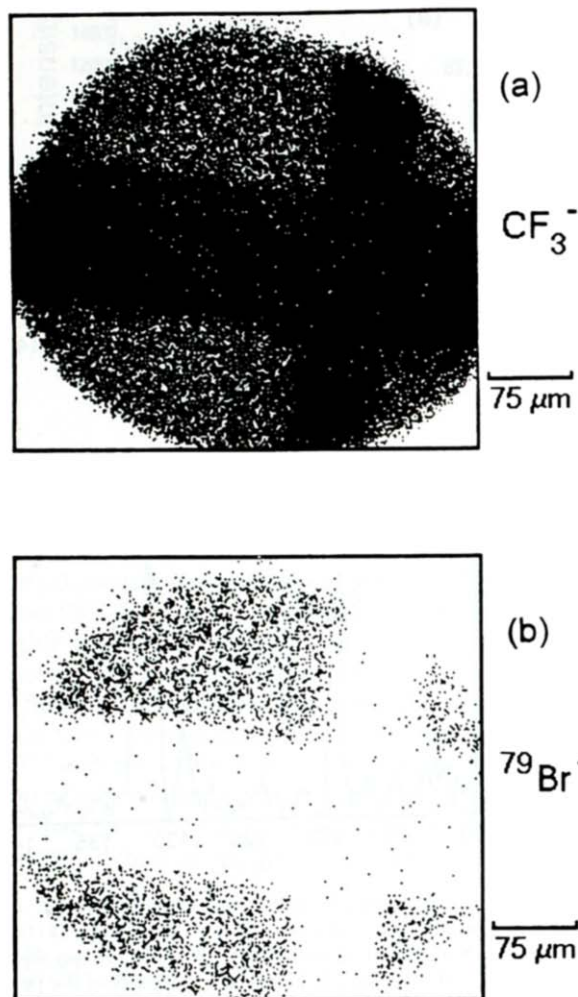


Figure 5. TOF-SIMS images (25 keV, Ga⁺) of (a) CF₃⁻ and (b) Br⁻ from a C⁸¹Br⁺ and CH₂⁷⁹Br⁺ doublet (*m/z* 93) bombarded fluorinated SAM surface. The ion beam was patterned with a copper grid (50 mesh, 0.01-in. wire diameter). Note the decrease of CF₃⁻ intensity and increase of Br⁻ intensity in exposed relative to unexposed areas. (Darker regions represent higher intensity of species monitored.)

surface can be accompanied by its substitution with chlorine, as indicated by the presence of CFCI⁺ and CF₂Cl⁺ in the scattered ion beam. The surface itself was not examined in these experiments; however, model gas-phase ion-molecule reactions with a PCI⁺ projectile and C₆F₁₄ collision gas were investigated. Product ion spectra showed the formation of PCIF⁺, PCIF₂⁺, C₆F₁₂⁺, and C₆F₁₂Cl⁺ as major features (Figure 8). This last species represents the gas-phase Cl-for-F halogen substitution product and, as such, appears to arise by a process that is the analog of the process that takes place upon ion-surface collision.

A limited amount of thermochemical data that pertain to these ion-surface reactions is available. For example, the gas-phase reaction, CH₂Br⁺ + CF₄ → CH₂F⁺ + CF₃Br is endothermic by 43 kcal/mol [37]. In spite of its probable unfavorable thermochemistry, CH₂Br⁺ was found to undergo the Br-for-F substitu-

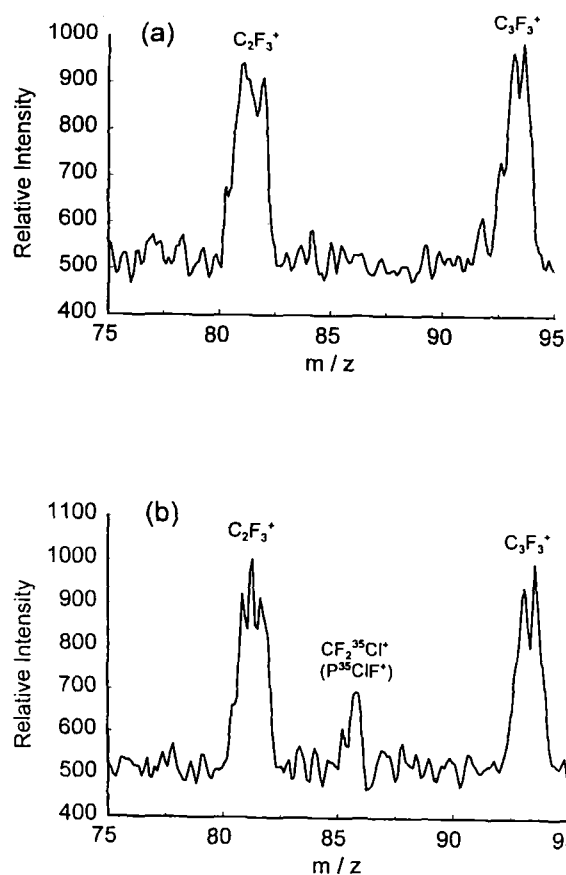


Figure 6. Partial chemical sputtering spectra recorded upon 60-eV collision of ¹³²Xe⁺ at a fluorinated SAM surface (a) before and (b) after bombardment with 60-eV P³⁵Cl₃⁺ projectile for 20 min. Note the appearance of the peak at *m/z* 85 in (b). Alternative species given in parentheses are discussed in the text.

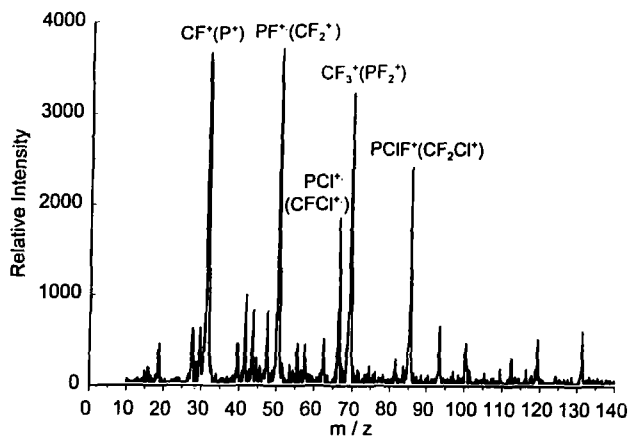


Figure 7. Scattered ion mass spectrum recorded upon 60-eV collision of a P³⁵Cl⁺ projectile at a fluorinated SAM surface. Note the relatively high intensity of ion-surface reaction products PF⁺ and PCIF⁺. Alternative species given in parentheses are discussed in the text.

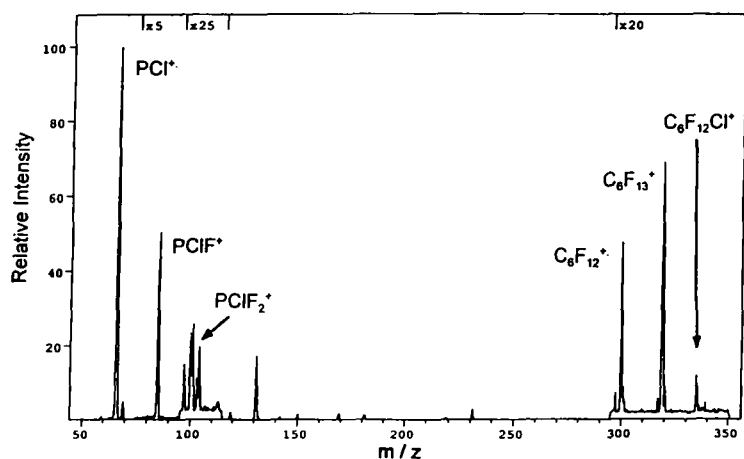


Figure 8. Partial product ion mass spectrum recorded upon gas-phase reaction between $P^{35}Cl^{+}$ and C_6F_{14} at 2-eV translational energy and 1-mtorr pressure in the second quadrupole in a triple quadrupole mass spectrometer. Note the presence of peaks at m/z 300 and 335 due to $C_6F_{12}^{+}$ and $C_6F_{12}Cl^{+}$, respectively.

tion reaction in ion-surface collisions. This observation is in agreement with previous studies that indicate that F-SAM surfaces have a high efficiency of translational to internal energy transfer [24] and that thermodynamically unfavorable ion-surface reactions can be driven by the translational energy of the projectile ion [28].

Conclusion

The most important finding of this study is that chemically selective surface modification can be achieved by "soft landing" of ion beams. The results point toward the development of a form of chemical writing on surfaces in which patterns are written in the appropriate chemical functional groups. Subsequent reactions at the modified surfaces, that use more conventional techniques, might then be used to further modify these sites. Exciting possible applications for such materials can be expected to exist in nanomagnetism, nonlinear optics, molecular electronics, and structure-based molecular design [38-41].

Some information on the mechanisms of ion-surface reactive collisions is already available [42-47] from studies of the scattered ionic products. In particular, the fluorine atom abstraction process has been suggested to occur by an oxidative addition mechanism. In this study, we have shown that associated selective chemical changes are induced at the surface and that surface analysis can reveal the processes that take place. Of particular interest is the case of formal halogen transfer between the projectile ion and the surface, for which evidence is presented from examination of both the scattered ion beam and the surface. In addition, the analogous gas-phase reaction has been shown to occur. More detailed mechanistic studies, such as confirmation of the proposed fluoronium ion intermediate, still await exploration.

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