

Low-Energy Collisions of Group IIIA, IVA, VA, VIA, and VIIA Ions with Fluoroalkyl SAM Surfaces: Reactions, Chemical Sputtering, and Mechanistic Implications†

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Low-energy (10–90 eV) atomic ions of group IIIA, IVA, VA, VIA, and VIIA elements (E) undergo reactions with a fluorinated self-assembled monolayer surface to give fluoride cations, EF_n^+ . One, two, or three fluorine atoms can be abstracted. Ion/surface reactions are also observed with polyatomic ions of these elements, but in general, atomic ions are much more reactive and react at lower collision energies than the corresponding polyatomic species. The higher collision energies reflect increased energy consumption needed for fragmentation. Most of the ion/surface reactions investigated in this study are endothermic and are driven by the translational energy of the projectile, although there remains a high degree of thermochemical control over reactivity. Thermochemical control over neutralization of the primary beam is also evident; ions with high recombination energies, like N^+ and O^+ , completely neutralize at the fluorocarbon surface. In addition, certain general trends in behavior have been observed for elements within the same periodic group. The reactions occur in single scattering events, and they are not associated with electron transfer from the surface to the ion, as are the well-known hydrogen and alkyl group abstractions by organic radical ions. In most cases, the ion/surface reaction seems to occur after, or in concert with, dissociation of the polyatomic projectile. When multiple abstractions occur, the fluorine atoms can be lost from the same alkyl chain; evidence for this is the enhanced intensity of specific sputtering products, e.g. $C_3F_3^+$, upon collisions of ions such as Sb^+ , which readily abstract more than one fluorine atom. Ion/surface reactions in which new bonds are formed in the surface alkyl group are also observed; such reactions give rise to unusual product ions which are sensitive to the chemical nature of the projectile. Examples include chlorine-for-fluorine atom substitution at the surface and PCF_2^+ formation in P^+ collisions. These processes suggest the possibility of selective chemical modification of the outermost monolayers of surfaces using low-energy reactive ion beams.

Introduction

When low-energy polyatomic ions interact with surfaces, a variety of processes occur. These include inelastic scattering,^{1–14} charge exchange,^{15,16} particle deposition,¹⁷ and chemical sputtering.^{18,19} The extent to which a particular phenomenon occurs depends on a number of factors, among which the chemical nature of the surface and the projectile is particularly important. Inelastic collision may be followed by dissociation of the scattered ion, a process known as surface-induced dissociation (SID).¹ SID has been the focus of particular interest,²⁰ due to its value in ion structural studies and its potential as an alternative to gas phase collision-induced dissociation (CID) in chemical analysis. However, as a wider variety of surfaces have been examined in an attempt to improve the efficiency of SID and to maximize translational to vibrational (T→V) energy transfer, more cases of reactions between the projectile and the surface have been encountered.^{8,21–28} Consequently, interest is developing in understanding these ion/surface reactions and in attempting to utilize their potential for characterization of functional groups at interfaces. Their possible application in surface science is made attractive by the fact that low-energy ions sample only the top-most layers of the surface. For example, in a recent investigation, we used the method of ion/surface reactions to obtain information on the microscopic surface structure of a liquid.²⁶

A well-known ion/surface reaction is abstraction of a hydrogen atom by an impinging radical cation (M^+), giving rise to a $(M + H)^+$ ion in the mass spectrum.²¹ In the case of highly

unsaturated ions, such as C_2HN^+ , abstraction of up to four hydrogen atoms has been observed.²¹ Similarly, alkyl group additions to the projectile ion (up to six carbon atoms) have also been shown to take place.^{10,29} Hydrogen and alkyl groups can originate from an adsorbate at the surface, or they may represent an integral part of the surface itself. For example, the pyrazine molecular ion picks up a CD_3 group from a deuterated self-assembled monolayer (SAM) surface, while the same projectile abstracts a CH_3 group from the corresponding hydrocarbon SAM surface or from hydrocarbon adsorbed to a metal surface.²² Molecular dynamics simulations suggest that these reactions, involving single-bond formation, occur on a very short time scale, on the order of several picoseconds.¹⁰ A number of experimental findings,^{22,23,27} as well as theoretical calculations,²⁴ point to a reaction mechanism initiated by electron transfer from the surface species to the projectile ion. Fragmentation within the adsorbate may then yield a surface-derived fragment ion, a process known as chemical sputtering,¹⁹ or the fragment ion might be captured by the neutralized projectile to form the ion/surface reaction product.

Abstraction of fluorine atoms from fluorinated SAM surfaces has been shown to represent another common ion/surface reaction.^{23,26} Wysocki and co-workers observed fluorine abstraction by the molecular ion of benzene to form ionized fluorobenzene;^{16,24} I^+ , CH_3I^+ , and Xe^+ have also been shown to abstract fluorine.²⁷ In a recent study, we have shown that ion/surface collisions at fluorinated SAM surfaces can give rise to multiple bond formation; up to five bonds can be formed in the case of the W^+ projectile.²⁸ A number of monatomic and polyatomic transition metal ions were used as projectiles in these low-energy collision experiments. Although the time scale of this interaction is not fully understood, it is clear that the ion spends sufficient

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time at the surface, so as to interact with multiple fluorine atoms, and it leaves with a very low translational energy. Angle-resolved ion/surface scattering experiments have suggested that the ions undergo multiple atom abstraction in a single collision event;²⁸ support for this conclusion comes from experiments in which an analog to the proposed intermediate in the surface study is generated and mass-selected in the gas phase and its behavior is characterized.²⁸ There is also evidence, from the translational energy dependence of fluorine atom abstraction, that electron transfer is not a prerequisite for reaction,²⁸ as it is for hydrogen and alkyl group transfer.²⁷

This paper is concerned with the abstraction of fluorine atoms from a fluorinated SAM surface by atomic and polyatomic ions of group IIIA, IVA, VA, VIA, and VIIA elements. The study extends the reactive collision experiments carried out with transition metal ions at fluorinated SAM surfaces.²⁸ Many of the questions asked in relation to that study are also valid here. How general is the abstraction of multiple atoms from surfaces? Does it depend on the valence of the projectile ion? Do ions of a particular chemical group abstract the same number of fluorine atoms under identical conditions? Does spatial extension of orbitals play an important role in these ion/surface reactions? How important are thermochemical considerations in these processes? Can the translational energy of the projectile drive endothermic reactions? Do projectile ions accumulate at the surface, so that they can be desorbed subsequently by the action of another projectile? If multiple abstractions occur, are the atoms abstracted all derived from a single alkyl chain? If this were the case, multiple abstraction reactions might give rise to distinctive sputtering products. What does one know about the sequence of events occurring in a reaction between a polyatomic projectile and the surface? Does the intact molecular ion abstract atom(s) from the surface and subsequently fragment, or do its fragments undergo abstraction? Does electron transfer occur during the ion/surface reactive collision event?

Experimental Section

Experiments were performed using a four-analyzer BEEQ mass spectrometer, specially designed to study ion/surface collisions.³⁰ A mass- and energy-selected ion beam (first two analyzers) is directed to the surface located in a high-vacuum scattering chamber. Prior to impinging at the surface, the beam is decelerated to set its collision energy. The energy and mass distribution of the scattered products are analyzed by the remaining two analyzers (EQ), which are mounted on a rotating rail. This geometry allows one to vary the incident beam angle, as well as to study the angular distribution of the scattered products. The surface can be rotated so that the incident angle can also be varied independently. The base vacuum in the scattering chamber was kept at 1×10^{-8} Torr. The primary ions were generated by 80 eV electron impact. Variation of electron energy in the range from 16 to 250 eV did not affect the pattern of abundances of the abstraction products. An incident angle of 55° (with respect to the surface normal) and a scattering angle of 90° (with respect to the primary beam direction) were used in all experiments.

The target employed in this study was a self-assembled fluorinated alkyl monolayer supported on a gold film through a sulfur linkage, $\text{CF}_3(\text{CF}_2)_{11}(\text{CH}_2)_2\text{S}-\text{Au}$, prepared in C. Chidsey's laboratory, as described elsewhere.^{31,32} The surface was rinsed in ethanol before being admitted into the scattering chamber. No deterioration of the surface, as judged by the scattered ion spectra, was observed after day-long experiments. All chemicals were commercial grade and used without pretreatment. Except in the cases of ^{13}C , S, Cl, I, and Br, chlorides were used to generate atomic and molecular projectile ions. Methane $^{13}\text{C}\text{H}_4$ was used as the source of $^{13}\text{C}^+$, S^+ was derived

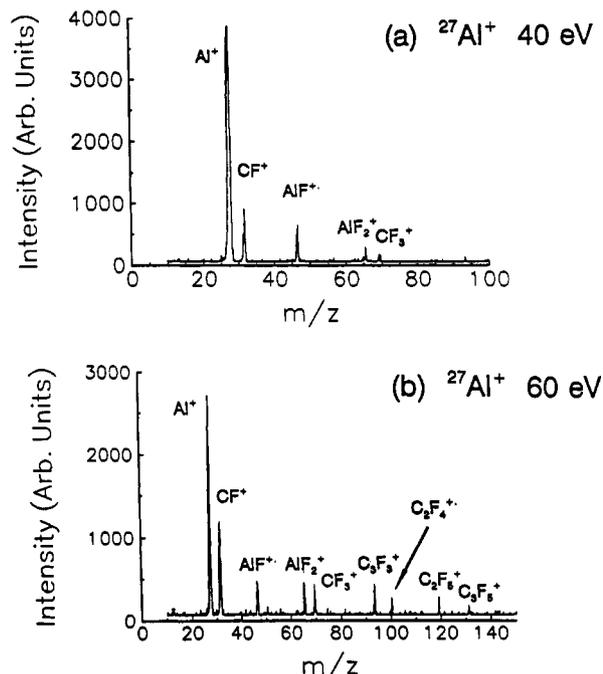


Figure 1. Scattered ion mass spectra obtained upon collisions of Al^+ projectile ions at a fluorinated SAM surface at (a) 40 eV and (b) 60 eV collision energy.

from $\text{C}_2\text{H}_5\text{SH}$, S_2^+ was generated from $(\text{C}_2\text{H}_5\text{S})_2$, and Cl-, Br-, and I-containing ions were generated from the corresponding methane dihalides. Oxygen and nitrogen ions were formed from the corresponding gaseous elements.

Results and Discussion

Group IIIA. Figure 1a shows the scattered ion mass spectrum obtained when a 40 eV Al^+ ion beam impinges on the fluorinated self-assembled monolayer surface. In addition to the reflected projectile itself, the spectrum shows two ion/surface reaction products, AlF^+ and AlF_2^+ , as well as well-known peaks due to chemical sputtering of the surface, CF^+ (m/z 31) and CF_3^+ (m/z 69). As the collision energy is increased to 60 eV (Figure 1b), the abundance of the ion/surface reaction products increases along with the corresponding increase in intensity of the sputtering peaks.

If one makes the assumption that the thermochemistry of the ion/surface reaction is approximately the same as that of the corresponding gas phase reaction, for which thermochemical data are available,³³ abstraction of a single fluorine atom in the case $\text{Al}^+ + \text{C}_2\text{F}_6 \rightarrow \text{AlF}^+ + \text{C}_2\text{F}_5$ is estimated to be 53 kcal/mol endothermic, while the direct abstraction of two fluorine atoms from a single chain, leading to the formation of AlF_2^+ and C_2F_4 is 45 kcal/mol exothermic (Table 1). On the other hand, sequential abstraction of two fluorine atoms from two different alkyl chains would be endothermic by a total of 8 kcal/mol, unless interchain C—C bond formation occurred, in which case the reaction would be exothermic by ca. 78 kcal/mol. Entropic considerations suggest that Al^+ ion will preferentially undergo double fluorine atom abstraction from the same alkyl chain, but energetically favorable interchain reactions are not excluded.

In addition to atomic Al^+ , all polyatomic projectile ions derived from AlCl_3 , except the molecular ion itself, were tested and found to undergo F atom abstraction. Projectile ions with increased number of atoms, e.g. AlCl^+ , AlCl_2^+ , and AlCl_3^+ , require increased collision energy in order to yield ion/surface reaction products in comparable abundance to the Al^+ projectile. This behavior is true for all of the polyatomic projectiles investigated in this study; it may simply reflect the fact that polyatomic projectiles

TABLE 1: Thermochemical Data for Elements Investigated in This Study^a

element (E)	recom- bination energy, eV	heat of reaction, kcal/mol					
		heat of formation, kcal/mol			single F abstraction ^b	double F abstraction	
		E ⁺	EF ⁺	EF ₂ ⁺		from 2 chains ^c	from 1 chain ^d
Al	5.98	216	161	8	53	8	-45
Ga	5.99	203	167	<i>e</i>	72	<i>e</i>	<i>e</i>
Tl	6.10	184	199	<i>e</i>	123	<i>e</i>	<i>e</i>
C	11.26	431	271	214	-52	-1	-54
Si	8.15	295	163	108	-24	29	-24
Ge	7.20	272	166	132	2	76	23
Sn	7.34	242	142	140	8	114	61
Pb	7.42	218	154	162	44	160	107
N	14.53	448	<i>e</i>	275	<i>e</i>	<i>e</i>	-10
N ₂	15.58	395	<i>e</i>	315	<i>e</i>	<i>e</i>	119
P	10.49	317	212	90	3	-11	-64
Sb	8.64	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>
Bi	7.29	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>
O	13.62	374	320	308	54	150	97
O ₂	12.07	278	294	<i>e</i>	124	<i>e</i>	<i>e</i>
S	10.36	305	236	161	39	72	19
S ₂	9.36	246	194	176	56	146	93
Se	9.75	279	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>
Se ₂	8.70	236	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>
Te	9.01	255	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>
Cl	12.97	328	280	269	60	157	104
Br	11.81	299	257	<i>e</i>	66	<i>e</i>	<i>e</i>
I	10.45	267	222	<i>e</i>	63	<i>e</i>	<i>e</i>

^a From ref 33. ^b Refers to the reaction $E^+ + C_2F_6 \rightarrow EF^+ + C_2F_5$.
^c Refers to the reaction sequence $E^+ + C_2F_6 \rightarrow EF^+ + C_2F_5$; $EF^+ + C_2F_6 \rightarrow EF_2^+ + C_2F_5$, without bond formation between surface chains. ^d Refers to the reaction $E^+ + C_2F_6 \rightarrow EF_2^+ + C_2F_4$. ^e Data not available.

release a larger fraction of their translational energy into the internal modes. The scattered products observed upon collisions of Al-containing projectile ions at three different collision energies are summarized in Table 2; the abundances of all major sputtering peaks are also included. As can be seen, no sputtering takes place at a collision energy of 20 eV; while the actual threshold varies with the nature of the projectile, sputter ions generally begin to occur between 30 and 40 eV collision energy. Their further increase in abundance with increase in collision energy is very pronounced, and in some of the spectra, the sputtering peaks become dominant at energies as low as 60 eV. A feature worth noting is the fact that C₂- and C₃-containing sputtering peaks have significant abundance only at collision energies of 60 eV and higher. This may be an indication that their formation

requires deeper penetration of the projectile into the surface. The peaks due to C₃F₃⁺ and C₃F₅⁺ are usually weak; their substantial abundance in the spectra, shown in Table 2, can therefore be related to the fluorine abstraction reaction, not to simple chemical sputtering. From a number of examples in the present study, it can be seen that an increase in abundance of these ions coincides with processes in which significant fluorine abstraction is also observed; multiple fluorine abstraction tends to create unsaturated sites in the surface alkyl chains, hence the enhancement of abundance of unsaturated fluorocarbon sputtered ions.

Two other elements of group IIIA were examined. The study of Ga⁺ (*m/z* 69) was hampered due to coincidence of its mass and the mass of a major sputtered ion, CF₃⁺. The other element studied was thallium, which did not show any fluorine atom abstraction up to a collision energy of 90 eV; TlCl⁺ exhibited similar behavior. The lack of reactivity of Tl⁺ ions can be rationalized by the fact that the formation of TlF⁺ from Tl⁺ and C₂F₆ is a highly endothermic reaction (estimated to be 123 kcal/mol).

Group IVA. All the group IVA elements have been investigated. The results obtained with C⁺ and other carbon-containing ions are difficult to interpret, since the scattered products can, in principle, include contributions from carbon atoms originating both from the projectile and from the surface. This problem was overcome by using the ¹³C⁺ projectile; these experiments are of special mechanistic value, since they allow a direct comparison between the abstraction reaction and the chemical sputtering processes. Abstraction of fluorine by the projectile ¹³C⁺ yields ¹³CF⁺, while the corresponding sputtered ion has the composition ¹²CF⁺. Experiments at different collision energies show that abstraction of a fluorine atom takes place at energies as low as 10 eV. This should come as no surprise, since the process is 52 kcal/mol exothermic (Table 1). As the collision energy is increased, the relative abundance of ¹³CF⁺ peak increases in comparison to the reflected ¹³C⁺ projectile. The threshold for chemical sputtering, on the other hand, occurs between 30 and 40 eV, as evidenced by the appearance of the ion ¹²CF⁺, which subsequently, at collision energies of 60 eV and above, becomes the dominant product. The abstraction of two F atoms from a single chain by the C⁺ projectile should be exothermic by 54 kcal/mol, a value very close to that for single fluorine abstraction. However, scattered ion mass spectra show no evidence of the formation of CF₂⁺ ions; this observation, and a similar one for the Si⁺ projectile, point to the fact that favorable thermochemistry is not the only determining factor for the outcome of an ion/surface reactive collision. In particular, the less favorable entropy requirements can suppress the thermochemical advantage of certain processes.

TABLE 2: Scattered and Sputtered Product Ions Resulting from Collisions of Group IIIA Projectiles at a Fluorinated SAM Surface^a

projectile	collision energy, eV	scattered products (relative abundance)										sputtered products (relative abundance)							
		Tl	Al	AlF	AlCl	AlF ₂	AlCIF	AlCl ₂	AlCl ₂ F	AlCl ₃	CFCl ^b	CF ₂ Cl ^b	CF	CF ₂	CF ₃	C ₃ F ₃	C ₂ F ₄	C ₂ F ₅	C ₃ F ₅
Al	20		100	5		1													
	40		100	15		5						25		3	1				
	60		100	15		15						45	3	15	15	8	8	4	
AlCl	20		100	10	80	20													
	40		100	25	20	5	10					10		5	2				
	60		100	20	10	10	10												
AlCl ₂	20																		
	40		30	10	65	5	25	100				4	15	1	15		1		
	60		100	55	70	35	70	60	5		15	35	85	30	80	10	25	15	20
AlCl ₃	20																		
	40		10		30	20													
	60		60	25	70	15	70	100	5		10	40	50	10	80	5	20	8	10
Tl	20-90	100																	
TlCl	20-90	100																	

^a All species listed are singly charged positive ions. ^b These products are present in most of the spectra of chlorine-containing projectiles, usually at very low abundance. They are deleted from other Tables to avoid overcrowding of information.

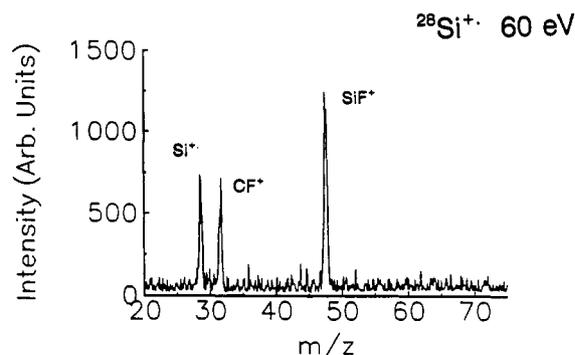


Figure 2. Scattered ion mass spectrum obtained upon collisions of 60 eV Si^+ projectile ions at a fluorinated SAM surface.

Besides carbon, silicon is the only element among those investigated for which single fluorine atom abstraction is exothermic. However, unless interchain C—C bond formation occurs, there is no additional thermochemical advantage to the formation of SiF_2^+ , since both single and double F abstraction are exothermic by 24 kcal/mol (Table 1). Figure 2 shows the scattered ion mass spectrum obtained when a beam of $^{28}\text{Si}^+$ impinges on the fluorinated SAM surface. The only ion/surface reaction product seen in the spectrum is SiF^+ , and its abundance exceeds that of the reflected Si^+ beam at all collision energies examined (Table 3). The identity of the product was checked by mass selecting the heavier isotope of silicon, $^{29}\text{Si}^+$. When the collision energy was increased to 60 eV, SiF^+ was still the only product observed. The absence of the SiF_2^+ product can be rationalized on the same basis as the absence of the corresponding carbon reaction product discussed above. The presence of the CF^+ sputtering peak, while other commonly encountered sputtered ions like CF_2^+ and CF_3^+ are virtually absent, is an unexpected observation; this behavior was encountered with some other projectiles (e.g. Al^+), although to a smaller extent. A more detailed examination of this phenomenon established that the CF^+ peak is present in the scattered ion spectra of Si^+ and SiCl^+ at collision energies as low as 20 eV. This is below the threshold for chemical sputtering by almost all other projectiles, and it appears that a mechanistically different form of sputtering is involved. The process is closely associated with the ion/surface reaction and is considered a form of reactive sputtering. The process suggested to take place is elaborated later in connection with the discussion of the Br^+ projectile, which exhibits similar behavior.

Projectile ions SiCl_n^+ ($n = 0-2$), derived from SiCl_4^+ , yield SiF^+ upon collision at the surface. As the number of chlorine atoms in the projectile increases, the relative abundance of SiF^+ products obtained at the same collision energy decreases; alternatively, a constant yield of SiF^+ product can be achieved by employing higher collision energies. This behavior reflects the energy requirement for the fragmentation of the polyatomic projectile to give lower mass ions, particularly Si^+ , which is the most reactive of all silicon-containing ions in collision with the fluorinated SAM surface. In addition to the atomic ion itself, intact SiCl^+ and SiCl_2^+ also exhibit fluorine abstraction, as opposed to SiCl_3^+ and SiCl_4^+ , which do not yield intact fluorine addition products.

The formation of GeF^+ from Ge^+ and C_2F_6 is almost thermoneutral (2 kcal/mol endothermic), while the direct abstraction of two fluorine atoms with concomitant double-bond formation is 23 kcal/mol endothermic (Table 1). Consequently, the formation of GeF_2^+ is not expected to be a probable process, and it is not observed. Sn^+ and Pb^+ also show exclusively single fluorine abstraction, an expected result in view of the relevant thermochemistry: formation of SnF^+ and PbF^+ is 8 and 44 kcal/mol endothermic, respectively, while double fluorine atom

TABLE 3: Scattered Product Ions Resulting from Collisions of Group IVA Projectiles at a Fluorinated SAM Surface^a

projectile	collision energy, eV	scattered products ^b (relative abundance)							
		C	CF	CCl	CClF	CCl ₂	CCl ₂ F	CCl ₃	
C	20	95	100						
	40	100	60						
	60	20	100						
CCl	20	5	15	100					
	40	20	40	100					
	60	25	100	60					
CCl ₂	20			100		85			
	40		10	100	3	25	2		
	60		40	100		10	2		
CCl ₃	20					10		100	
	40			30		80	2	100	
	60		10	100	2	30	5	30	
¹³ C	20	¹³ C	¹³ CF	¹² CF					
	40	100	40						
	60	25	80	100					
Si	20	Si	SiF	SiCl	SiClF	SiCl ₂	SiCl ₂ F	SiCl ₃	
	40	70	100						
	60	60	100						
SiCl	20	85	100	90	10				
	40	80	100	55	3				
	60	30	100	10	5				
SiCl ₂	20	10	100	15		85	60		
	40	5	40	100			15		
	60	20	100	70					
SiCl ₃	20					90	35	100	
	40		5	45	5	90	45	100	
	60		55	100	15	50	95	45	
SiCl ₄	20					3	1	100	
	40			5		35	10	100	
	60		15	65	10	75	55	100	
Ge	20	Ge	GeF	GeCl	GeClF	GeCl ₂	GeCl ₂ F	GeCl ₃	
	40	20	100						
	60	10	100						
GeCl	20	25	100						
	40	5	20	100					
	60	5	100	95					
GeCl ₂	20	25	100	50					
	40			100					
	60		25	100					
GeCl ₃	20	10	55	100					
	40			10		30		100	
	60		10	100	5	70	15	45	
GeCl ₄	20		30	100	5	20	10	5	
	40		5	100	5	20	10	5	
	60		10	100	25	5		25	
Sn	20	Sn	SnF	SnCl	SnClF	SnCl ₂	SnCl ₂ F	SnCl ₃	
	40	30	100						
	60	30	100						
SnCl	20	35	100	45					
	40	10	20	100					
	60	1	5	100	3	25	5	10	
SnCl ₂	20	10	40	100	5	5	5	2	
	40	10	40	100	5	5	5	2	
	60	5	20	100	2	15	2	5	
SnCl ₃	20								
	40								
	60								
SnCl ₄	20								
	40								
	60								
Pb	20	Pb	PbF	PbCl	PbClF				
	40	100	30						
	60	60	20	100	10				

^a All species listed are singly charged positive ions. ^b Sputtered ions have been deleted for reasons of clarity. Also not included are low-intensity peaks due to CFCl^+ and CF_2Cl^+ observed in most spectra of chlorine-containing projectiles.

abstraction requires 61 kcal/mol for tin and 107 kcal/mol for lead ion projectiles (Table 1).

Throughout the present study, certain similarities in behavior of elements within the same group have been noted; group IVA is a case in point. All five elements have been investigated,

TABLE 4: Scattered Product Ions Resulting from Collisions of Group VA Projectiles at a Fluorinated SAM Surface^a

projectile	collision energy, eV	scattered products ^b (relative abundance)														
		P	PF	PCF	PCl	PF ₂	PCF ₂	PCIF	PCICF	PCl ₂	PCIF ₂	PCICF ₂	PCl ₂ F	PCl ₃	PCl ₂ F ₂	PCl ₃ F
N ₂	30–90	none														
P	20	85	100			25										
	40	100	100			20										
	60	100	95	15		80	10									
PCl	20	15	10		100			25								
	40	100	100		75	20		30								
	60	100	100		50	85		65								
PCl ₂	20				10			5		100						
	40	10	35		100	15		70		100						
	60	65	80		95	85		100	5	80	3	8				
PCl ₃	20							100					1	50		3
	40	2	3		60	2		25		100			10	10		2
	60	15	35		85	40		90		100	2		5	3	1	1
Sb			Sb	SbF	SbCl			SbF ₂	SbClF	SbCl ₂	SbCl ₃					
	20		100	30												
	40		75	100				75								
SbCl	20		30	5	100											
	40		60	100	85			40	65							
	60		60	100	70			85	75							
SbCl ₂	20				15					100						
	40		15	10	100			40	60							
	60		35	70	100			45	95	65						
SbCl ₃	20				2					100	3					
	40				60			15	100							
	60		10	20	100			10								
Bi			Bi	BiF	BiCl	BiF ₂	BiClF	BiCl ₂	BiCl ₃							
	20		100	20												
	40		100	80		15										
BiCl	20		50		100											
	40		100	50	65	5	25									
	60		100	60	30	5										
BiCl ₂	20		5		50			100								
	40		45	10	100		20	65								
	60		100	45	100	5	35	25								
BiCl ₃	20				15			100	5							
	40		20		100		10	80								
	60		75	25	100		30	35								

^a See footnote a in Table 2. ^b See footnote b in Table 2.

although the amount of data available for lead is limited, due to poor sensitivity. Some of the common features that group IVA elements share are (i) all form EF⁺ product ions, none forms EF₂⁺; (ii) there is a monotonic decrease in the exothermicity of EF⁺ formation in going down the group; (iii) for all elements (except Pb), the intensity of EF⁺ > E⁺ at all collision energies, presumably reflecting the favorable thermochemistry for single fluorine abstraction; (iv) in addition to EF⁺, the only other ion/surface reaction products observed for all the elements are EClF⁺ and ECl₂F⁺; and (v) they all yield CF⁺ as the major (often exclusive) surface-sputtered ion.

Group VA. The results obtained for group VA elements are presented in Table 4. Collisions of nitrogen ions with the fluorinated SAM surface do not yield any observable ion/surface reaction products. Furthermore, for both N⁺ and N₂⁺, hardly any reflected projectile could be detected in the scattered ion spectra. This behavior has been observed before¹⁹ with other projectiles and is attributed to the high neutralization efficiency of the nitrogen projectiles, due to their high recombination energies (14.53 and 15.58 eV for N⁺ and N₂⁺, respectively). In comparison, phosphorous P⁺, the element below nitrogen in group VA, has a recombination energy (RE) of 10.48 eV only, and both the reflected projectile and products of ion/surface reactions are observed in its scattered ion mass spectra. The spectrum recorded upon 60 eV collisions of P⁺ is shown in Figure 3. It should be noted that some phosphorous peaks coincide in mass with surface-sputtering peaks, e.g. P⁺ and CF⁺ at *m/z* 31, PF⁺ and CF₂⁺ at

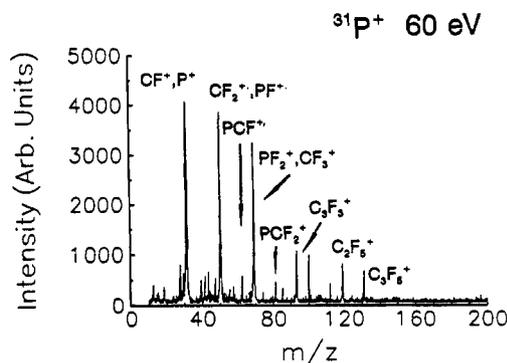


Figure 3. Scattered ion mass spectrum obtained upon collisions of 60 eV P⁺ projectile ions at a fluorinated SAM surface. Note the possibility of coincident species at *m/z* 31, 50, and 69.

m/z 50, and PF₂⁺ and CF₃⁺ at *m/z* 69. Therefore, the corresponding ion assignments and abundances in the spectra of all phosphorous-containing ions should be viewed as approximate only. Abstraction of one F atom is 3 kcal/mol endothermic, while the simultaneous acquisition of two F atoms from the same surface chain is 64 kcal/mol exothermic (Table 1). Both single and double fluorine abstraction yield intense peaks. A new feature in some of the P⁺ spectra is the presence of PCF⁺ and PCF₂⁺ ions, products of projectile atom for fluorine substitution in the alkyl chain, with subsequent C—C bond cleavage. While Sb⁺ and Bi⁺ do not form such products, elements of groups VIA and VIIA

TABLE 5: Scattered Product Ions Resulting from Collisions of Group VIA Projectiles at a Fluorinated SAM Surface^a

projectile	collision energy, eV	scattered products ^b (relative abundance)																		
		O ₂	S	SF	SCF	S ₂	S ₂ F	Se	SeF	SeCF	SeCl	SeF ₂	SeCF ₂	SeClF	SeCl ₂	Se ₂	Se ₂ F	Se ₂ Cl	Se ₂ Cl ₂	
O ₂	30	100																		
	90	none																		
S	20	100	15																	
	40	100	30	15																
	60	100	60	35																
S ₂	40	70	20		100	10														
Se	20	100	30																	
	40	90	100	25		25	10													
	60	55	100	60		25	10													
SeCl	40	40	40		100	5	5	20												
	60	65	80	50	100	20	20	30												
SeCl ₂	20				55									100						
	40	15	10		100						15			30						
	60	30	40		100	10					40			30						
Se ₂	20	5													100	5				
	40	25	15												100	20				
	60	35	35	20					15	10					100	25				
Se ₂ Cl	20	3				20									100				70	
	40	10	10			35					5				100	10			15	
	60	30	20	15		40	15	10	10	10					100	25			10	
Se ₂ Cl ₂	20					100								5	3	50	2		60	30
	40	5	1			100				3	5			5	50	2		40	5	
	60	25	25			100	25			20	10			80	10			20		
Te	40	100	85																	
	60	90	100	20						40	3									
	40	100	70			75	15				35									
TeCl	40	85	100	5		55	30	2		30	5									
	60	15				100				25				45						
TeCl ₂	40	35	70			100	20			45				20						
	60	1	1			100				2				100	1				5	
TeCl ₃	40	20	15			100	2			30				70	5				5	
	60																			

^a See footnote *a* in Table 2. ^b See footnote *b* in Table 2.**TABLE 6: Scattered Product Ions Resulting from Collisions of Group VIIA Projectiles at a Fluorinated SAM Surface^a**

projectile	collision energy, eV	scattered products ^b (relative abundance)																	
		CCl	CFCI	CF ₂ Cl	C	CH	CH ₂	CF	CHF	CH ₂ F	Br	BrC	BrCH	BrCH ₂	BrF	BrCF	BrCHF	BrCF ₂	BrC ₂ F ₃
Cl	60	75	10	100															
	20									100								70	
	40									20					10	20		100	10
Br	60										25			15	20		100	10	
	20					40					100				5		30		
BrC	20					100					100				25				
	60	30				100					100				25		30		
BrCH	20					30		20				100				50			
	60					40		25				100			15		15	5	
BrCH ₂	20					60	5		15				100						
	40					95	25		50		15		100		1		3		
	60					95	30		30		15		100		5		15		
I	20																		
	40																5		
	60																50	15	
IC	20																		
	40					10			100								3		
	60					45			40								10		
ICH	20					70			35										
	60					10			10								15		
ICH ₂	20					55	35		35	25		100							
	40	10				1	3		3			100							
	60	25				15	20		20			100	3						
ICH ₂	60	85	25			70	50	20	25	100	30	2				5			

^a See footnote *a* in Table 2. ^b See footnote *b* in Table 2.

exhibit the corresponding peaks in large abundance (Tables 5 and 6). Note the large relative abundance of C₃F₃⁺ and C₃F₅⁺ sputtered ions (Figure 3), paralleling the large intensity of PF⁺

and PF₂⁺ products, as previously discussed for Al. Of the three phosphorous chloride ions, only PCl⁺ and PCl₃⁺ abstract fluorine from the surface; indeed, the behavior of PCl₃⁺ comes as a surprise,

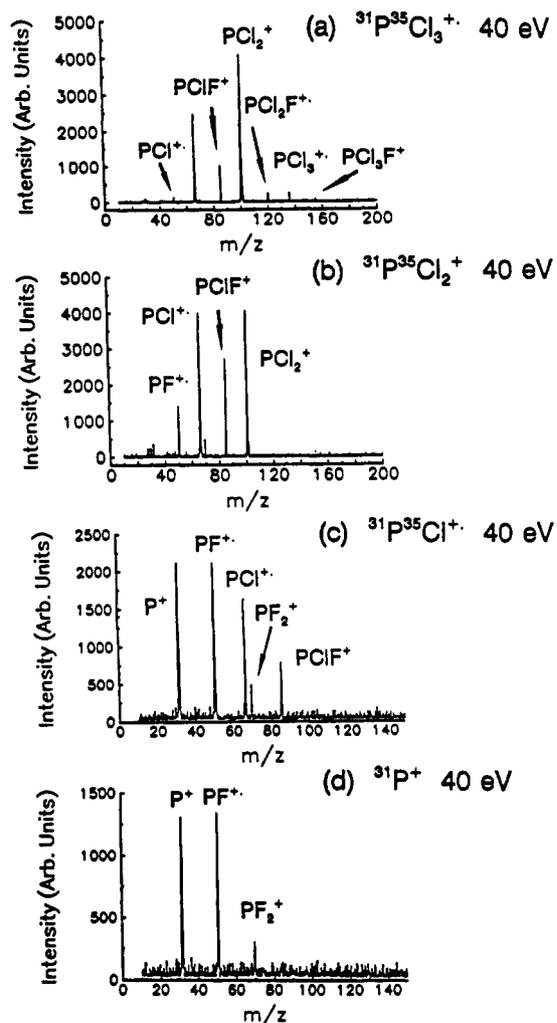


Figure 4. Scattered ion mass spectra obtained upon 40 eV collisions of (a) PCl_3^+ , (b) PCl_2^+ , (c) PCl^+ , and (d) P^+ projectile ions at a fluorinated SAM surface.

since it is the only molecular ion in this study that undergoes fluorine atom abstraction without fragmentation (Figure 4). It is interesting to note that while PCl_2^+ projectile *does not* react with fluorine from the surface to give PCl_2F^+ at any collision energy, a PCl_2F^+ product *is* observed in the spectrum of PCl_3^+ projectile (Figure 4a). This could be due to fragmentation of PCl_3F^+ , or to the reaction of PCl_3^+ , which reacts with the surface by Cl-for-F exchange reaction. In most cases of polyatomic projectiles, fragmentation seems to take place before, or in concert with, the reaction with surface species.

No thermochemical data are available for the mono- and difluorides of antimony and bismuth. Figure 5 shows the scattered ion mass spectra of 60 eV ion beams of two isotopes of Sb; note the good agreement between the abundances of all peaks in the two spectra, a measure of the reproducibility of these experiments. The exceptionally large abundance of SbF_2^+ product suggests that the process of abstracting two F atoms should have a favorable thermochemistry, comparable to that of the phosphorus reaction (Table 1). Of the three chloride ions, only SbCl^+ shows fluorine abstraction. The projectiles SbCl_2^+ and SbCl_3^+ do not react as such, but rather fragment to yield Sb^+ and SbCl^+ , both of which are reactive species that do abstract fluorine. Very similar behavior characterizes bismuth-containing ions (Table 4).

An interesting feature of Figure 5 is the presence of peaks at m/z values 15, 27, 29, 39, 41, 43, 55, 57, etc., which represent hydrocarbon ions that have been sputtered by the projectile. These ions originate from hydrocarbon adsorbate and can be very abundant at metal surfaces, especially under poor vacuum

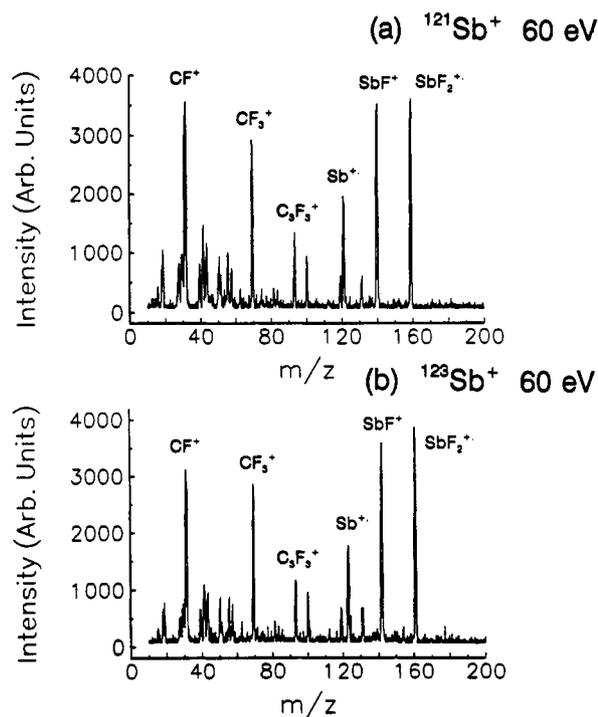


Figure 5. Scattered ion mass spectra of two isotopes of Sb^+ projectile ions obtained upon 60 eV collisions at a fluorinated SAM surface.

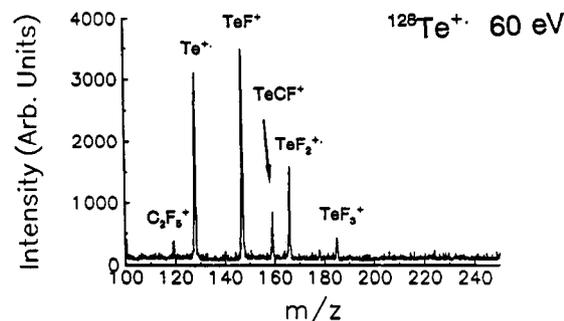


Figure 6. Partial scattered ion mass spectrum obtained upon 60 eV collisions of $^{128}\text{Te}^+$ projectile ions at a fluorinated SAM surface.

conditions.²⁰ They are usually absent or present in very low abundance in experiments employing fresh fluorinated surfaces;¹⁸ as the surface suffers some damage after prolonged ion bombardment, hydrocarbon adsorbates tend to bind to the damaged sites, and corresponding sputtering peaks appear in the spectra.²⁴ Wysocki et al. have used this phenomenon as a means of assessing the extent of surface damage.³⁴ These ions appear in low abundance in a number of the spectra shown here, but are particularly abundant in the case of antimony.

Group VIA. All the elements of group VIA, except oxygen, show fluorine abstraction products. The behavior of oxygen is similar to that of nitrogen; O^+ undergoes complete neutralization at the surface (RE 13.62 eV), while O_2^+ yields a reflected ion signal, but no fluorine abstraction reaction is observed. This can be attributed to the unfavorable thermochemistry: formation of O_2F^+ is estimated to be endothermic by 124 kcal/mol.

No thermochemical data are available for the higher group VIA fluoride cations, SF^+ , SeF^+ , and TeF^+ . The reactivity increases in going from sulfur toward tellurium (Table 5). Thus, S^+ forms SF^+ and the corresponding Se^+ projectile abstracts one or two F atoms, while Te^+ can abstract up to three fluorines (Figure 6). In addition, SCF^+ , SeCF^+ , SeCF_2^+ , TeCF^+ , and TeCF_2^+ are produced in reactions which are the result of bonding by the projectile ion to the surface with associated C—C bond cleavage in the alkyl chain.

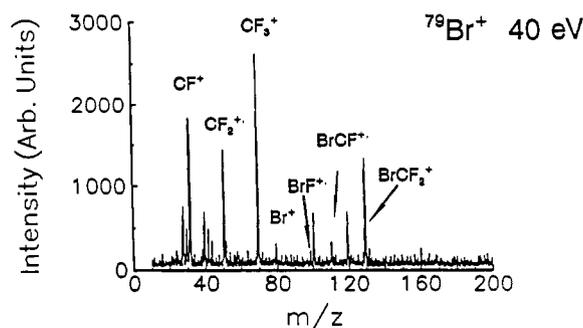


Figure 7. Scattered ion mass spectrum obtained upon 40 eV collisions of $^{79}\text{Br}^+$ projectile ions at a fluorinated SAM surface.

Group VIIA. Abstraction of fluorine atoms by group VIIA elements is highly endothermic: formation of ClF^+ by 60 kcal/mol, BrF^+ by 66 kcal/mol, and that of IF^+ by 63 kcal/mol (Table 1). Neither element forms a difluoride in low-energy ion/surface collisions; thermochemical data are available for ClF_2^+ only, and its formation is estimated to be 104 kcal/mol endothermic. At lower collision energies, Cl^+ ion yields extremely weak signals in the scattered ion spectra; neutralization of the projectile seems to predominate, in agreement with the high value of the recombination energy (12.97 eV). Moving down the group, the signals for Br^+ and I^+ projectiles become increasingly abundant and the scattered ion mass spectra exhibit a rich chemistry (Table 6). In the 40 eV product ion mass spectrum for Br^+ projectile (Figure 7), the most intense product is BrCF_2^+ , and this is the case for other collision energies, as well. By contrast, in the spectrum of I^+ , IF^+ is the most abundant product. Incoming Br^+ displaces F from the alkyl fluoride and yields the product of reactive sputtering BrCF_2^+ (vide infra), while this reaction channel is less important in competition with simple fluorine abstraction in the I^+ case. The difference is probably due to the larger size of I^+ . The 20 eV collision energy spectra of bromine-containing ions are presented in Figure 8; most striking is the richness of these spectra, unusual for such low-energy collisions. A large number of experiments, with widely differing projectiles, has established that no sputtering peaks appear in 20 eV spectra at fluorinated SAM surfaces.^{18,23} Nevertheless, Figure 8a, which shows the spectrum obtained with the Br^+ projectile, shows two unexpected peaks, attributed to CF_3^+ and C_2F_5^+ , in addition to the reflected Br^+ and the reaction product BrCF_2^+ . The CF^+ peak, which usually appears in surface sputtering in comparable abundance with CF_3^+ , is totally absent. These observations can be rationalized by a mechanism in which Br^+ chelates the terminal C_2F_5 group. When C=C bond cleavage occurs, the loosely bound complex $\text{C}_2\text{F}_5\text{Br}^+$ can fragment in several ways, yielding Br^+ , BrCF_2^+ , CF_3^+ , and C_2F_5^+ . Each of these products is observed in the spectrum. CF_3^+ and C_2F_5^+ ions formed in the above process do not represent chemical sputtering peaks in the usual sense, i.e. products of charge exchange of the projectile with the surface species, followed by ejection of an ionized fragment. Consequently, we refer to this process as reactive sputtering, to emphasize the fact that a sputtering product was formed as a result of an ion/surface reaction. Entirely different events occur when CBr^+ projectiles impinge at the surface (Figure 8b). The projectile ion picks up a fluorine atom from the surface, yielding CBrF^+ as the product. The only other peak observed in the spectrum is CF^+ , suggestive of normal surface sputtering. However, there is now no trace of the major sputtering ion CF_3^+ ! These observations are in agreement with a process that involves an intermediate in which the CBr^+ projectile is attached to a surface fluorine atom. Upon breaking of a C—F bond, this results in the formation of CBrF^+ , which can be detected as such or else can fragment to lose bromine, yielding the CF^+ ion. Thus, CF^+ in this case represents the product of projectile fragmentation, not surface sputtering, a conclusion verified with ^{13}C -labeled projectiles.

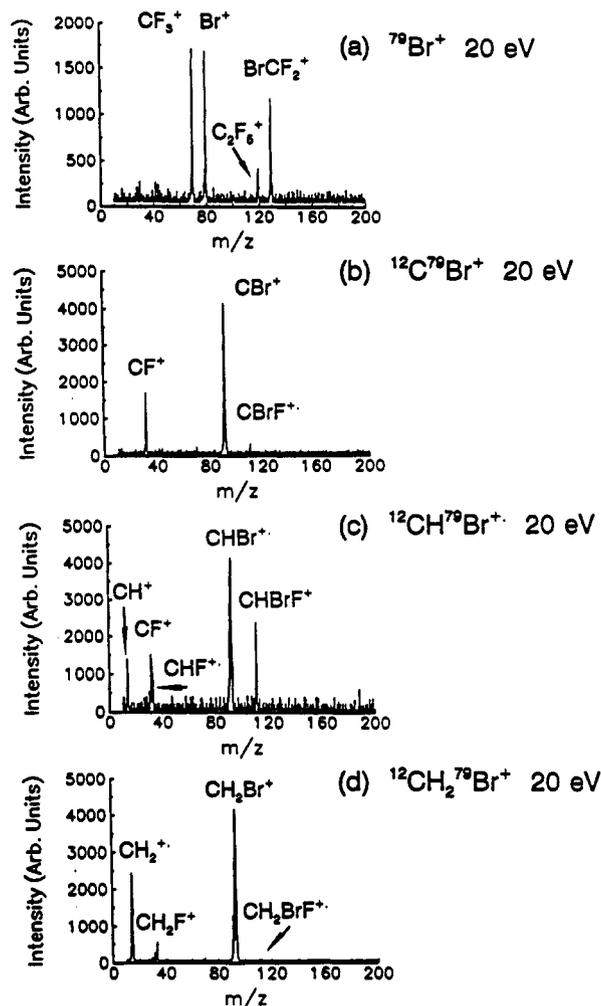


Figure 8. Scattered ion mass spectra obtained upon 20 eV collisions of (a) Br^+ , (b) CBr^+ , (c) CHBr^+ , and (d) CH_2Br^+ projectile ions at a fluorinated SAM surface.

Support for the proposed mechanism comes from the behavior of two additional bromine-containing projectiles, the 20 eV spectra of which are shown in Figure 8c,d. The CHBr^+ projectile gives rise to CHF^+ , CF^+ , and CH^+ ions, consistent with fragmentation of an initially formed CHBrF^+ species. Likewise, the CH_2Br^+ projectile yields a low-abundance CH_2BrF^+ product, which upon fragmentation, gives CH_2F^+ and CH_2^+ as the main products. The corresponding spectra of iodine-containing projectiles (Figure 9) exhibit similar features. It should be noted that reactive sputtering is best distinguished at low collision energies; at higher energies, other processes, including conventional chemical sputtering, tend to dominate. Thus, for example, the 40 eV spectrum of Br^+ ion (Figure 7) already shows the presence of all major sputtering peaks.

Some Common Characteristics. There are several characteristics common to the polyatomic ions investigated: (i) they abstract only a single F atom from the surface (two in rare cases, and then only in very low abundance); (ii) molecular ions, as a rule, do not exhibit fluorine addition (PCl_3^+ is a notable exception); (iii) in a number of cases, while ECl_nF^+ product is not observed in the spectrum of ECl_n^+ projectile, it is observed in the spectrum of ECl_{n+1}^+ or ECl_{n+2}^+ projectiles. For example, GeCl_2^+ projectile does not yield a GeCl_2F^+ product upon collisions at the surface; however, GeCl_2F^+ is recorded in the scattered ion mass spectra of both GeCl_3^+ and GeCl_4^+ projectiles (Table 3). These observations point to the importance of a leaving atom or group that can take away excess energy and thus stabilize the product.

Further Thermochemical Considerations. The C—F bond is stronger than most E—F bonds of group IIIA–VIIA elements,

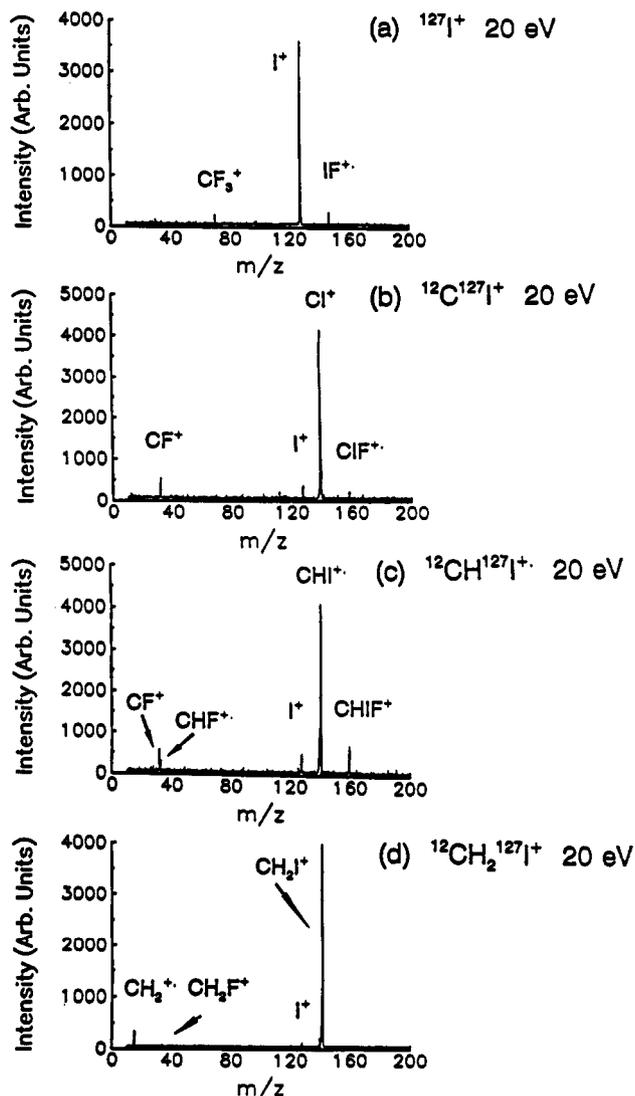
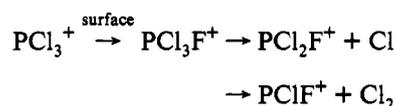


Figure 9. Scattered ion mass spectra obtained upon 20 eV collisions of (a) I^+ , (b) ClI^+ , (c) CHI^+ , and (d) CH_2I^+ projectile ions at a fluorinated SAM surface.

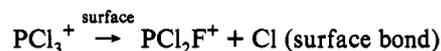
and, consequently, the formation of most monofluorides by ion/surface reactions is endothermic, as shown in Table 1. Such reactions must be driven by the translational energy of the projectile, i.e. by $\text{T} \rightarrow \text{V}$ energy conversion, and would therefore be expected to occur with low efficiency. In the present study, however, there are numerous examples in which products of ion/surface reactions exhibit very large abundance, indeed, representing the base peak in some spectra. Nevertheless, as a general observation, thermochemical dictates are obeyed: exothermic and close to thermoneutral processes are usually more abundant, while endothermic reactions occur with low efficiencies, or are absent altogether. One way of assessing the relevant thermochemistry is by comparing the abundance ratio of monofluoride product to that of the scattered atomic projectile. For example, in the 20 eV collision energy spectrum of Al^+ , the ratio AlF^+/Al^+ is 0.05, while the corresponding spectrum of Ge^+ displays a ratio GeF^+/Ge^+ of 5.0, reflecting the fact that AlF^+ formation is 53 kcal/mol endothermic, while that of GeF^+ is almost thermoneutral (2 kcal/mol endothermic). Similar correlations are observed for the formation of other monofluorides from the corresponding atomic projectiles. The absence of any reaction of Ti^+ ion (abstraction of a single F atom would be 123 kcal/mol endothermic) is an example of how very large energy requirements can prevent a process from being observed altogether. This reaction was attempted by increasing the collision energy to 90 eV, but no reaction product could be detected, pointing to the

fact that extremely unfavorable thermochemistry cannot always be compensated by $\text{T} \rightarrow \text{V}$ conversion. While the experimental observations generally agree with thermochemical data, some results are unexpected: for example, neither CF_2^+ nor SiF_2^+ are observed in the scattered ion mass spectra of C^+ and Si^+ projectiles, although both processes would be highly exothermic. In these cases, as well as in some others, data cannot be explained on the basis of thermochemical considerations alone, and it is obvious (and reasonable) that entropic requirements play a role.

Mechanism. A basic mechanistic question is, when fragments of polyatomic projectiles yield ion/surface reaction products, does projectile fragmentation precede, accompany, or follow reaction with the surface? Our earlier studies on other nonorganic systems provided evidence that, in many cases, projectile fragmentation takes place upon collision at the surface and that the fragments thus formed undergo reaction with the surface species.^{27,28} A significant fraction of the present results is compatible with such an interpretation. For example, the scattered ion spectrum of AlCl^+ projectile shows products due to reactions of both Al^+ and Cl^+ with the surface. It seems reasonable, therefore, to assume that AlCl^+ projectile fragments upon collision at the surface, yielding either Al^+ or Cl^+ products; the former can react with the surface to form AlF^+ and AlF_2^+ , while the latter can yield CFCl^+ and CF_2Cl^+ products. Except for AlF^+ , none of the above ion/surface reaction products would be expected from fragmentation of AlClF^+ , which should be the case had the "reaction followed by fragmentation" sequence been involved. On the other hand, the absence of PCl_2F^+ product from the spectrum of PCl_2^+ projectiles, and its presence in the spectrum of PCl_3^+ projectile, in which a PCl_3F^+ product is also observed, suggests that an alternative sequence may take place: PCl_3^+ reacts with fluorine first, and the product subsequently dissociates to give PCl_2F^+ and lower mass fragments. In this case, the intermediate adduct ion seems to be stable enough so as to actually be observed in the scattered ion spectrum, together with the products of its further fragmentation:



However, one can visualize a third mechanism in which fragmentation and reaction take place simultaneously:



viz., a form of Cl-for-F halogen exchange between ion and surface.

Collision Energy Effects. In most of the experiments discussed above, scattered ion mass spectra obtained at low collision energies exhibit ion/surface reaction products, as well as products of surface-induced dissociation. As the collision energy is increased, sputtered ions occur, and, eventually, they dominate the spectra. In a few cases, at extremely low collision energies, ion/surface reaction products were observed, while SID products were completely absent. The general observation for these systems is that the energy requirement for the processes encountered in ion/surface interactions follow the order ion/surface reactions < SID < chemical sputtering. This is a reasonable conclusion based on the underlying thermochemistry. Ion/surface reactions involve the formation of certain bonds along with breaking of other; the net result is that the energy requirement should typically be lower than that for a SID process, which involves only bond cleavage. On the other hand, chemical sputtering, in addition to bond cleavage, involves prior ionization of the surface species, which is endothermic by the difference between the ionization energy of the surface and that of the neutral projectile. The different thresholds of chemical sputtering and ion/surface reaction suggest that electron transfer, which is a necessary

condition of chemical sputtering, need not occur in the course of ion/surface fluorine abstraction reactions. Previous studies have provided evidence that hydrogen and hydrocarbon group pickup from the corresponding surfaces does proceed through an electron transfer mechanism.^{22-24,27} Contrary to this, the experimental evidence suggests that ion/surface reactions in which fluorine atoms are abstracted from the surface do not involve electron transfer.^{24,27,28}

Surface Modification. In the course of ion/surface interactions, bonds at the surface are being broken and atoms and groups removed, which results in the formation of radical sites. These sites may be involved in recombination, elimination of certain atoms or groups, or chemical reactions with appropriate species present at the interface, such as neutralized projectiles or their fragments. In the present experiments, in which a number of chlorine-containing species have been used as projectiles, it was observed that chlorine can efficiently bind to the radical sites created by the removal of fluorine. The CFCl^+ and CF_2Cl^+ ions thus formed were repeatedly observed in the scattered ion mass spectra (Table 2). That these species were permanently bound to the surface was confirmed in an experiment in which the surface, after exposure to SiCl_4^+ projectiles, was bombarded with 60 eV Xe^+ ions. Among other species, CF_2Cl^+ ions were observed, pointing to the fact that the fluorinated surface had indeed been chemically modified. The same result was subsequently confirmed by high-resolution SIMS imaging of the SiCl_4^+ -bombarded surface.³⁵ Bromine and iodine were shown to exhibit the same behavior. In fact, although the existence of the covalently bound species to the surface radical sites has not been examined for elements other than halogens, it is interesting to note that of all of the elements investigated in this study those in the upper right part of the periodic table (i.e. P, S, Se, Te, Cl, Br, I) give ECF^+ and ECF_2^+ ions as products in their scattered ion mass spectra, which could be an indication of their tendency to bind to the surface radical sites created at the surface upon fluorine atom abstraction. The pronounced nonmetallic character of those elements suggests the importance of covalent bonding in these processes.

Conclusions

Atomic and molecular projectiles of group IIIA, IVA, VA, VIA, and VIIA undergo several types of interactions with fluorinated SAM surfaces. These include ion/surface reactions in which multiple fluorine atoms are abstracted from the fluorinated surface in low-energy collisions, fluorine substitution reactions at the surface, and chemical sputtering of surface-derived ions. We also note the occurrence of sputtering events in which ions derived from the surface group are released into the gas phase in a process which does not involve the usual charge exchange mechanism (viz., chemical sputtering), but is rather the result of ion/surface reactions followed or accompanied by fragmentation of the products. Most of the attention has focused on those ion/surface reactions which result in new bond formation in the scattered ion, among which F atom abstraction is paramount. This reaction, although normally endothermic, occurs with unusually high efficiency, the abstraction products often constituting the base peaks in the scattered ion mass spectra.

Atomic ions of group IIIA–VIIA elements react with fluorinated surfaces by abstracting one or two fluorine atoms; only Te^+ was found to yield a weak signal for TeF_3^+ product. This behavior is in contrast to the collisions of low-energy polyatomic organic ions with the same surfaces, where multiple fluorine atom abstraction is never observed.²³ On the other hand, transition metal ions undergo this process readily, with additions of up to five F atoms being recorded.²⁸ The reactivity of a particular ion depends on the availability of vacant orbitals, thermochemistry, and geometry of the reactants at the surface. There seems to be no direct correlation between valence and number of species

abstracted. For example, although the elements of group IVA have a valence of four, only single fluorine atom abstraction is seen. In this respect, groups IIIA–VIIA ions behave differently from the transition metal ions where the maximum number of fluorine atoms abstracted is usually $n - 1$, n being the maximum oxidation number of the metal.^{26,28} Although spatial extension of the orbitals increases the probability of multiple atom abstraction, an increase in the ionic radii alone is not enough for multiple atom abstraction; the thermochemistry must not be too unfavorable. The study shows a number of trends in reactivity shared by elements within a group. When multiple abstractions occur, there is evidence, through unique sputtering products, e.g. enhanced abundance of C_3F_3^+ in such cases as Al^+ , that they can occur from a single alkyl chain. This does not exclude the accompanying, thermochemically more favorable, possibility of cross-linking of chains through new C—C bond formation. Note, however, that such events are more difficult to detect by the methods used here, since subsequent release of the modified surface groups requires even more extensive bond cleavages.

Turning to the details of the mechanism of the fluorine abstraction reaction, the lack of dependence of relative ion abundances on ion dose eliminates the possibility that material is deposited at the surface and released by a subsequent collision. Evidence has been provided in the case of the analogous transition metal ion collisions that transfer of fluorine atoms from the surface to the projectile takes place in a single collision event,²⁸ this conclusion has been supported by subsequent gas phase collision experiments which show that a single alkyl chain can transfer multiple fluorine atoms to a W^+ ion.²⁸ The results of the present experiments are also consistent with a single scattering event at the surface. Although the time scale of interaction is not available, the thermochemistry demands that the reaction is definitely not occurring at two or more well-separated surface species. Abstraction of two fluorines is much more favorable thermochemically when both F atoms originate from the same alkyl chain (last column in Table 1); this reaction is favored by 53 kcal/mol over the corresponding process in which two F atoms are abstracted from two different chains (second from last column, Table 1). Abstraction of two fluorine atoms from adjacent chains, with subsequent C—C bond formation, is thermochemically the most favorable of all processes, although there is no direct evidence that it occurs. It seems likely that the fluorine atom(s) abstraction reaction proceeds via formation of a short-lived collision complex. Such a complex could involve the projectile undergoing multiple collisions with a small group of atoms confined to the near-surface region (due to the limited penetration depth of the low-energy projectile). In the course of this collision sequence, energy would be exchanged with the surrounding fluorocarbon groups, and in favorable cases, some of these collisions would be reactive, leading to fluorine atom pickup by the projectile or its fragmentation products. On a less important question, that of the sequence of processes whereby fluorinated fragment ions are generated, the evidence is that the molecular projectiles appear to react in concert with or after fragmentation.

A further mechanistic question is whether the fluorine atom abstraction occurs by an electron transfer process, in analogy with the hydrogen and alkyl transfer ion/surface reactions discussed in the Introduction,^{22-24,27} or whether it occurs by a direct oxidative addition mechanism.³⁶ The data do not exclude the electron transfer mechanism in all cases, but there is also clear evidence that reaction can occur at energies well below the threshold for chemical sputtering and hence that electron transfer is *not* involved.

The study has provided more information on the well-known process of chemical sputtering. It is found that when the projectiles and chemical sputtering products have similar masses, sputtering is enhanced. This mass effect is shown to exist with a number of projectiles,¹⁸ and it suggests that impulsive collisions might be

involved, viz., that the necessary electron transfer occurs at the repulsive wall of the potential energy surface describing the ion/surface interaction.¹⁹ In addition, there seems to be another mechanism by which surface groups can be ejected as gas phase ions. This process, termed reactive sputtering, appears not to be due to simple chemical sputtering of surface species, but actually involves an ion/surface reaction. For example, the formation of CF_3^+ on collisions of certain Br-containing projectile ions is due to reactive sputtering. As expected, such processes are extremely sensitive to the chemical nature of the projectile, since they depend on specific ion/surface chemical interactions. Closely related are those ion/surface reactions which involve release of a *chemically modified* form of the surface group as a gas phase ion. A number of cases have been encountered in this study, including CFBr^+ formation on collision of Br^+ with the fluoroalkane surface. It is interesting to note that these ion/surface collisions occur at low energy and might be valuable in surface modification. Note, too, that the radical site created at the surface can be satisfied with a halogen atom provided as part of the projectile; for example, the surface of a fluorinated SAM is modified to produce $-\text{CBrF}_2$ head groups after the reaction. This species is detected in this study when released by C—C bond cleavage, and the process is of interest as a means of achieving selective chemical modification of the outermost monolayers of a surface. This kind of molecular surface engineering can be envisioned as a means to make new C—C bonds in order to achieve molecular growth at surfaces. It may be possible to attach an atom or group from an external source to the radical sites created on the surface as a result of ion/surface reactions. Preliminary experiments with surface imaging methods have shown that chlorine delivered from the projectile ion is bound to the surface,³⁵ and this is encouraging in respect to the goal of controlled chemical writing with ion beams on surfaces now envisioned.

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