

Reactions of Metal Ions at Fluorinated Surfaces: Formation of MF_n^+ ($\text{M} = \text{Ti}, \text{Cr}, \text{Fe}, \text{Mo}, \text{and W}; n = 1-5$)

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Abstract: Low-energy (<100 eV) ion/surface reactions of metal ions, Ti^{++} , Cr^{++} , Fe^{++} , Mo^{++} , and W^{++} , at a fluorinated self-assembled monolayer surface give fluorine-containing scattered ions, MF_n^+ , $n < 5$. The metal fluorides are the most abundant products in the scattered ion spectra. The single fluorine abstractions are all endothermic and driven by the projectile translational energy. Multiple fluorine abstraction occurs with high efficiency for Mo^{++} and W^{++} projectiles, where the thermochemistry is most favorable. Polyatomic projectile ions derived by partial fragmentation of the Cr, Mo, and W hexacarbonyls also yield metal fluoride scattered ions, in addition to more complex species formed by fluorine abstraction by ions which retain one or more carbon atoms or carbonyl groups. Fe- and Ti-containing projectile ions, bearing one or two cyclopentadienyl (Cp) groups, also exhibit fluorine abstraction products, with and without retention of a Cp group. TiCl_n^+ ($n = 1-4$) projectiles exhibit fluorine abstraction, as well. Similar fluorine abstraction products are generated upon collisions at a liquid perfluorinated polyether surface. Gas-phase ion/molecule reactions and thermochemical considerations suggest that multiple fluorine abstractions can occur by a direct reaction mechanism within a single scattering event and that multiple fluorine atoms are probably derived from a single fluorocarbon chain. Angle-resolved scattering data support a single-collision, multiple-atom abstraction mechanism. The scattered ions leave the surface with very low translational energy and collision energy variations suggest that in these ion/surface reactions, projectile dissociation is concerted with or occurs prior to fluorine abstraction. There is no evidence that electron transfer to the surface is involved, as it is in alkyl group abstraction reactions by ions at hydrocarbon surfaces.

Introduction

Ion/surface collisions at low energies (up to a few hundred electronvolts) may result in chemical reactions, in addition to a variety of other processes such as charge exchange, surface-induced dissociation (SID), electronic excitation, photon emission, particle deposition, and chemical sputtering.^{1,2} Some of these processes are of potential importance in surface science, catalysis, and materials science. Ion/surface reactions result in neutral or ionic scattered products, and analysis of these products can provide information on both the projectile and the surface chemical constitution. This method is potentially valuable for surface analysis because characterization might be based on highly specific chemical reactions; in addition, the ion beam is expected to preferentially sample the outermost atomic layers of the surface.³ In some cases, the method also appears to give information on the morphology of the surface at the atomic scale for condensed-phase systems.⁴

The occurrence of ion/surface reactions was demonstrated several years ago; pickup of one to four hydrogen atoms, as well

as alkyl groups of varying size, was observed.^{5,6} When using well-defined surfaces, such as a perdeuterated alkanethiolate self assembled monolayer (SAM) prepared on a gold film, a pyrazine ion beam was found to pickup D and CD_3 , clearly demonstrating the occurrence of ion/surface reactions.⁷ More recently, abstraction of hydrocarbon groups containing up to six carbon atoms was reported when polycyclic aromatic hydrocarbons (PAH) were used as projectiles.⁸ There is evidence that these alkyl group abstraction reactions proceed by electron transfer.⁹ Theoretical calculations^{8,10} suggest that the ions spend only extremely short periods of time at the surface (on the order of several picoseconds) during which these processes, which involve single bond formation, occur. Most recently, studies involving fluorinated SAM surfaces have established that abstraction of a fluorine atom occurs for some organic, halogen, and rare gas projectile ions.^{11,12}

There are a number of important questions we wish to address in connection with these processes. The first is concerned with the nature of the groups abstracted from the surface. Most of

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the reported cases of ion/surface reactions involve hydrogen atoms or hydrocarbon groups. In a recent study, we showed that a Cr^{++} ion beam can abstract a cyclopentadienyl group from a ferrocene-terminated SAM surface.¹³ It would be interesting to know how common this type of behavior is, i.e. whether covalent bonds at the surface are released readily and to what projectiles. The possibility that metal ions might abstract fluorine atoms from surfaces was tested using a group of transition elements which were also suitable for establishing the role of the metal-fluorine bond strength in facilitating these reactions. The second question concerns the number of species abstracted in a reactive collision. Ion/surface reactions generally involve formation of only one bond between the projectile and the abstracted species.² Apart from a rare case of multiple hydrogen atom pickup⁵ by the highly unsaturated ion C_2HN^+ and some cases in which low-abundance products appear to be generated by multiple fluorine atom abstraction,¹² no definite case is known where multiple bonds are formed as a result of a low-energy ion/surface interaction. One must therefore ask how likely is the possibility of multiple bond formation in a single collision? A third question is concerned with the nature of the projectile and whether complex metal ions behave similarly to the atomic projectiles. Finally, the mechanism of ion/surface reactions is of interest. The most studied reactions, those involving hydrogen or hydrocarbon group pickup from adsorbate covered metal surfaces and from organic surfaces (including SAMs), are believed to proceed via electron transfer.^{2,12} In particular, it has been proposed that these ion/surface reactions involve an initial electron transfer step, resulting in the formation of a neutral species, which subsequently binds to an ionic surface fragment. Fragmentation of the neutral projectile, prior to or in concert with the reaction, may also take place, leading to a variety of reaction products; any of these products can fragment further, contributing to the complexity of the phenomenon.

To begin answering these questions, we have carried out a series of experiments in which a number of transition metal ions were allowed to interact with a fluorinated self-assembled monolayer surface at different collision energies and scattering angles. The species chosen were Ti^{++} , Cr^{++} , Fe^{++} , Mo^{++} , and W^{++} , as well as a number of polyatomic ions containing these metals attached to carbonyl, cyclopentadienyl, or halogen ligands. All these projectiles exhibit multiple fluorine atom abstractions from the surface. The reactions of W^{++} and Mo^{++} yield products with as many as five and four fluorine atoms, respectively. This is the first reported observation of incorporation of multiple halogens into metal ions as a result of low energy ion/surface reactions.

Experimental Section

A four analyzer mass spectrometer, BEEQ¹⁴ (B = magnetic sector, E = electric sector, and Q = quadrupole mass analyzer), was employed to investigate ion scattering from the SAM surface. The first two sectors deliver a mass and energy selected ion beam to the surface via a decelerator, and the post collision analyzers, mounted on a rotating rail, yield the energy and mass distributions of the products that are scattered into selected angles. The surface can be rotated so that the incident angle can also be varied. The surface used in these experiments was a fluorinated self-assembled monolayer, prepared on a gold film and having the chemical composition $\text{CF}_3(\text{CF}_2)_{11}(\text{CH}_2)_2\text{S-Au}$, as described elsewhere.¹⁵ The SAM surface was rinsed in hexane before being admitted into the vacuum chamber. All compounds used in this study were commercial samples used as received. Ions were generated by 80 eV electron impact; the projectiles Cr^{++} , Mo^{++} , and W^{++} were generated from their hexacarbonyls, and Fe^{++} and Ti^{++} were obtained from ferrocene and TiCl_4^{++} , respectively.

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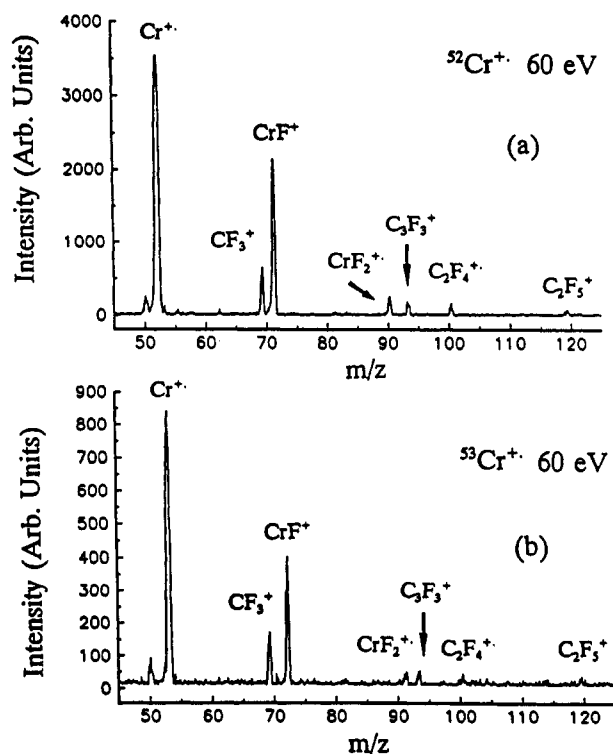


Figure 1. A portion of the scattered ion mass spectra obtained when 60 eV beams of (a) $^{52}\text{Cr}^{++}$ and (b) $^{53}\text{Cr}^{++}$ collide at the fluorinated SAM surface.

Typically, an ion beam of 0.2–1 nA was directed onto the target, where it impacted an area of ca. 3 mm². The scattering chamber was maintained at a pressure of 1×10^{-8} Torr throughout the measurement. No changes in the spectra were observed during the day-long measurements.

Normally, an incident angle of 55° (with respect to the surface normal) was used. The scattering angle was 90° (with respect to the direction of the incident beam). While recording the mass spectra, the electrostatic sector in the post collision region was adjusted to pass ions of the most probable translational energy. The band pass of the ESA was kept wide enough so that intensity variations were not due to this choice.

Some experiments were performed using a liquid perfluorinated polyether (PFPE), of the chemical composition $\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_{27}(\text{ave})\text{CF}_2\text{CF}_3$ (trade name, Krytox 1625, DuPont). The liquid was allowed to sheet across a stainless steel platchet to form a layer 8 μm thick. The liquid was degassed thoroughly before introduction into the collision chamber. Pressure in the chamber was maintained at 1×10^{-8} Torr. The liquid surface was remarkably clean, as revealed by ion/surface reactions with well-characterized projectiles and by chemical sputtering experiments.^{4,16}

Gas-phase ion/molecule reactions were studied using a Finnigan TSQ 700 triple quadrupole mass spectrometer. Mass selected positive ions $\text{W}(\text{CO})_n^{++}$ ($n = 0-6$), each produced by 70 eV electron impact on $\text{W}(\text{CO})_6$, were reacted with perfluorohexane, hexafluoroethane, or perfluoromethane in the second (rf-only) quadrupole. The product ions were recorded by scanning quadrupole 3; a number of different collision energies and collision gas pressures were examined.

All collision energy values are given in the laboratory frame of reference.

Results and Discussion

Figure 1a shows a partial scattered ion mass spectrum recorded when a 60 eV $^{52}\text{Cr}^{++}$ ion beam impinges on the fluorinated SAM surface. Apart from typical fluorocarbon ions due to chemical sputtering,⁹ the spectrum shows the presence of ion/surface reaction products CrF^+ and CrF_2^{++} at m/z 71 and 90, respectively. The identity of these ions was verified by experiments using $^{53}\text{Cr}^{++}$ ion projectiles (Figure 1b). Remarkably, CrF^+ and CrF_2^{++} products are obtained even when more complex Cr-containing ions, such as $\text{Cr}(\text{CO})_6^{++}$ or $\text{Cr}(\text{CO})_2^{++}$, are used as projectiles.

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In these cases, additional reaction products containing carbonyl groups, such as $\text{Cr}(\text{CO})\text{F}^+$, are also observed. In the case of the $\text{Cr}(\text{CO})_6^{++}$ projectile, products were observed only above 60 eV collision energy. The high threshold is reasonable in view of the fact that fragmentation of $\text{Cr}(\text{CO})_6^{++}$ to give Cr^{++} requires 15.4 eV,¹⁷ while the average internal energy that is expected to be deposited by 60 eV translational energy projectiles is only ca. 12 eV, considering the known 20% translational to internal energy conversion efficiency.^{11b} In agreement with the above arguments, CrF^+ and CrF_2^{++} products appear at a collision energy of just 30 eV when $\text{Cr}(\text{CO})_2^{++}$ projectiles are selected. Table 1 summarizes the ion/surface reaction products for various Cr-containing ions, as well as for other projectiles used in this study.

The reactions leading to CrF_n^+ formation are judged to be endothermic, if one utilizes the thermochemical data¹⁷ for the gas-phase reaction $\text{Cr}^{++} + \text{C}_2\text{F}_6 \rightarrow \text{CrF}_n^+ + \text{C}_2\text{F}_{6-n}^+$. In particular, CrF^+ formation is 56 kcal/mol endothermic, and subsequent addition of another fluorine from C_2F_6 to form CrF_2^{++} is endothermic by a further 90 kcal/mol. The one-step reaction $\text{Cr}^{++} + \text{C}_2\text{F}_6 \rightarrow \text{CrF}_2^{++} + \text{C}_2\text{F}_4$ is also endothermic (93 kcal/mol). Thus, thermochemistry suggests that fluorine abstraction reactions have to be driven by the translational energy of the projectile, and this is consistent with the fact that no reaction is seen with carbonyl-containing projectiles below 30 eV collision energy. In these cases, while there is sufficient translational energy to induce fragmentation of the projectile, the resulting atomic ions do not have sufficient energy to drive the endothermic fluorine abstraction reactions. Thermochemical considerations also show that abstraction of multiple fluorine atoms from the same alkyl chain is strongly favored compared to the corresponding processes involving two or more chains (Table 2). However, one should consider the possibility that, following the abstraction of two F atoms from two neighboring chains, a new C–C bond, connecting the two chains, could be formed. Using the C–C bond energy in C_2F_6 of 97 kcal/mol, one obtains the heats of reaction presented in the last column of Table 2. The gain of 97 kcal/mol for each pair of F atoms abstracted makes these processes energetically most favorable of all three considered; however, the actual distance between two neighboring fluorinated SAM chains is much too large for a C–C bond to bridge it (vide infra). Unfavorable entropy factors may be expected to greatly decrease the likelihood of this mechanism. Although the above thermochemical values are strictly valid for gas-phase processes only, their applicability as a guide to ion/surface reactions is justified by the fact that differences in heats of formation will tend to cancel, since reactants and products both involve similar surface-bound species.

Figure 2a shows a portion of the scattered ion spectrum recorded when a 60 eV beam of $^{98}\text{Mo}^{++}$ ions impinges upon the surface. As can be seen from the spectrum, ions due to fluorine abstraction are present in much larger abundance than in the Cr^{++} case. Indeed, MoF^+ constitutes the base peak in the entire mass spectrum, and MoF_2^{++} is of comparable abundance. As in the case of the Cr^{++} projectile, the identity of the product ions was verified using an isotopic ion, the $^{92}\text{Mo}^{++}$ isotope (Figure 2b). The most interesting aspect of these ion/surface reactions is the presence of multiple fluorine addition peaks; up to four fluorine atoms are abstracted by the Mo^{++} projectile (Table 1). Unlike the addition of C_nH_m species,² which require the formation of only one bond, these reactions involve formation of multiple bonds, a phenomenon not seen hitherto with atoms other than hydrogen, and even then limited to very few cases. Another interesting aspect of these reactions is the large abundance of the products. This is in contrast to the general behavior observed in ion/surface reactions, where the scattered ion/surface reaction products are typically of much lower abundance than the scattered projectile ion or its dissociation products.

Table 1. Products of Ion/Surface Reactions of Different Projectiles with a Fluorinated SAM Surface

projectile ion	collision energy (eV)	products ^{a-c}
Cr	200	CrF (100), CrF_2 (9)
	100	CrF (100), CrF_2 (25)
	60	CrF (100), CrF_2 (13)
	30	CrF (100), CrF_2 (20)
	30	CrF (100), $\text{Cr}(\text{CO})\text{F}$ (4)
$\text{Cr}(\text{CO})_2$	60	CrF (100), CrF_2 (15), $\text{Cr}(\text{CO})\text{F}$ (18)
	30	
	20	
Mo	60	MoF (100), MoF_2 (85), MoF_3 (53), MoF_4 (20), MoCF (20), MoCF_2 (3), MoCF_3 (3)
	30	MoF (100), MoF_2 (40), MoF_3 (20)
$\text{Mo}(\text{CO})_2$	60	MoF (100), MoF_2 (57), MoF_3 (20), MoF_4 (2), MoCF (2), MoCF_2 (2), MoCF_3 (3), MoCF_4 (1), $\text{Mo}(\text{CO})_2\text{F}_2$ (2)
	30	MoF (100), MoF_2 (10), MoF_3 (5), $\text{Mo}(\text{CO})\text{F}$ (8)
$\text{Mo}(\text{CO})_3$	60	MoF (100), MoF_2 (55), MoF_3 (21), MoF_4 (2), MoCF (3), MoCF_2 (4), MoCF_3 (5), MoCF_4 (1), $\text{Mo}(\text{CO})_2\text{F}$ (3), $\text{Mo}(\text{CO})_2\text{F}_2$ (2)
	30	MoF (100), MoF_2 (30), MoF_3 (10), MoF_4 (3), MoCF (2), MoCF_2 (4), MoCF_3 (15), MoCF_4 (3), $\text{Mo}(\text{CO})\text{F}$ (90), $\text{Mo}(\text{CO})_2\text{F}_2$ (1), $\text{Mo}(\text{CO})_2\text{F}$ (15)
$\text{Mo}(\text{CO})_6$	60	MoF (100), MoF_2 (25), MoF_3 (8), MoCF_2 (3), MoCF_3 (23), $\text{Mo}(\text{CO})\text{F}$ (73), $\text{Mo}(\text{CO})\text{F}_2$ (3), $\text{Mo}(\text{CO})_2\text{F}$ (5), $\text{Mo}(\text{CO})_2\text{F}_2$ (5), $\text{Mo}(\text{CO})_3\text{F}_2$ (3)
	30	
W	30	WF (5), WF_2 (50), WF_3 (100), WF_4 (30), WF_5 (3), WF_2C (3), WF_3C (5), WF_4C (3)
	30	WF (33), WF_2 (100), WF_3 (90), WF_4 (44), WF_5 (5), WCF_2 (12), WCF_3 (12), WCF_4 (8)
$\text{W}(\text{CO})_3$	60	WF (52), WF_2 (100), WF_3 (80), WF_4 (34), WF_2C (8), WF_3C (21), WCF_4 (7), $\text{W}(\text{CO})\text{F}$ (32), $\text{W}(\text{CO})_2\text{F}$ (3)
	30	WF (2), WF_2 (10), $\text{W}(\text{CO})\text{F}$ (60), $\text{W}(\text{CO})\text{F}_2$ (10), $\text{W}(\text{CO})_2\text{F}$ (100)
$\text{W}(\text{CO})_6$	60	WF (5), WF_2 (35), $\text{W}(\text{CO})\text{F}$ (100), $\text{W}(\text{CO})\text{F}_2$ (27), $\text{W}(\text{CO})_2\text{F}$ (54), WCF_3 (19)
	30	
$\text{Fe}(\text{Cp})_2$	60	FeF (100), FeF_2 (10), $\text{Fe}(\text{Cp})\text{F}$ (50)
	30	
$\text{Fe}(\text{Cp})$	30	FeF (100), $\text{Fe}(\text{Cp})\text{F}$ (10), FeF_2 (30)
	60	FeF (100), FeF_2 (6), FeCF (8)
Fe	30	FeF (100)
	30	$\text{Ti}(\text{Cl})\text{F}$ (20), $\text{Ti}(\text{Cl})_2\text{F}$ (100)
TiCl_4	60	$\text{Ti}(\text{Cl})\text{F}$ (100), $\text{Ti}(\text{Cl})_2\text{F}$ (55)
	30	$\text{Ti}(\text{Cl})\text{F}$ (57), $\text{Ti}(\text{Cl})_2\text{F}$ (100)
TiCl_3	60	TiF (40), TiF_2 (35), $\text{Ti}(\text{Cl})\text{F}$ (100), $\text{Ti}(\text{Cl})\text{F}_2$ (15), $\text{Ti}(\text{Cl})_2\text{F}$ (27)
	30	TiF (6), TiF_2 (5), $\text{Ti}(\text{Cl})\text{F}$ (100), $\text{Ti}(\text{Cl})\text{F}_2$ (12), $\text{Ti}(\text{Cl})_2\text{F}$ (34)
TiCl_2	60	TiF (93), TiF_2 (52), TiF_3 (5), $\text{Ti}(\text{Cl})\text{F}$ (100), $\text{Ti}(\text{Cl})\text{F}_2$ (12), $\text{Ti}(\text{Cl})_2\text{F}$ (5)
	30	TiF (100), TiF_2 (30), TiF_3 (4), $\text{Ti}(\text{Cl})\text{F}$ (83), $\text{Ti}(\text{Cl})\text{F}_2$ (5)
TiCl	60	TiF (100), TiF_2 (35), TiF_3 (5), $\text{Ti}(\text{Cl})\text{F}$ (29)
	30	TiF (100), TiF_2 (38), TiF_3 (2)
Ti	60	TiF (100), TiF_2 (52), TiF_3 (3)
	60	$\text{Ti}(\text{Cl})\text{F}$ (58), $\text{Ti}(\text{Cp})\text{F}$ (40), $\text{Ti}(\text{Cl})\text{F}_2$ (100), $\text{Ti}(\text{Cp})(\text{Cl})\text{F}$ (12), TiCl_2F (8), TiCl_2F_2 (14)
$\text{Ti}(\text{Cp})\text{Cl}_2$	30	$\text{Ti}(\text{Cl})\text{F}$ (100), $\text{Ti}(\text{Cl})\text{F}_2$ (20), $\text{Ti}(\text{Cl})_2\text{F}_2$ (30)
	60	TiF (55), TiF_2 (52), TiF_3 (10), $\text{Ti}(\text{Cl})\text{F}$ (100), $\text{Ti}(\text{Cp})\text{F}$ (19), $\text{Ti}(\text{Cl})\text{F}_2$ (47), $\text{Ti}(\text{Cl})_2\text{F}$ (8)
$\text{Ti}(\text{Cp})\text{Cl}$	30	$\text{Ti}(\text{Cl})\text{F}$ (40), $\text{Ti}(\text{Cl})\text{F}_2$ (100), $\text{Ti}(\text{Cl})_2\text{F}$ (15), $\text{Ti}(\text{Cp})(\text{Cl})\text{F}$ (15)
	60	TiF (54), TiF_2 (61), TiF_3 (20), $\text{Ti}(\text{Cl})\text{F}$ (100), $\text{Ti}(\text{Cp})\text{F}$ (9), $\text{Ti}(\text{Cl})\text{F}_2$ (20)
	30	TiF (15), TiF_2 (15), $\text{Ti}(\text{Cl})\text{F}$ (46), TiF_3 (2), $\text{Ti}(\text{Cp})\text{F}$ (21), $\text{Ti}(\text{Cl})\text{F}_2$ (100), $\text{Ti}(\text{Cl})\text{F}_3$ (4), $\text{Ti}(\text{Cp})(\text{Cl})\text{F}$ (2)

^a Only ion/surface reaction products are listed; other peaks, including SID fragments and sputtered ions, appear in some of the spectra. ^b Relative abundances (%) given in brackets are with respect to the most abundant ion/surface reaction product. ^c All projectiles and products listed are singly charged positive ions.

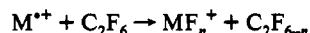
The MoF_n^+ product ions are also formed from other Mo-containing projectiles, such as $\text{Mo}(\text{CO})_6^{++}$, $\text{Mo}(\text{CO})_3^{++}$, and $\text{Mo}(\text{CO})_2^{++}$. In the case of these carbonyl projectiles, as in the Cr system, a larger collision energy is needed to form the MoF_n^+ ions, $\text{Mo}(\text{CO})_6^{++}$ displaying a higher energy threshold than $\text{Mo}(\text{CO})_3^{++}$ or $\text{Mo}(\text{CO})_2^{++}$ (Table 1). Thus, in the case of the hexacarbonyl projectile, no reaction is seen below 30 eV, while

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Table 2. Thermochemical Data for MF_n^+ Product Formation in Gas-Phase Reactions of M^{++} with C_2F_6 ^a

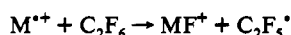
projectile	product	heat of reaction, kcal/mol		
		C=C bond formation ^b (when applicable)	no C—C bond formation ^c	C—C bond formation ^d
Cr ⁺⁺	CrF ⁺	56	56	
	CrF ₂ ⁺⁺	93	146	49
	CrF ₃ ⁺⁺	148	197	100
Mo ⁺⁺	MoF ⁺	36	36	
	MoF ₂ ⁺⁺	9	62	-35
	MoF ₃ ⁺⁺	41	90	-7
	MoF ₄ ⁺⁺	5	121	-71
	MoF ₅ ⁺⁺	e	175	-19
	MoF ₆ ⁺⁺	e	299	8
W ⁺⁺	WF ⁺	11	11	
	WF ₂ ⁺⁺	-34	19	-78
	WF ₃ ⁺⁺	-23	26	-61
	WF ₄ ⁺⁺	-71	35	-159
	WF ₅ ⁺⁺	e	58	-136
Ti ⁺⁺	TiF ⁺	18 ^f	18	
	TiF ₂ ⁺⁺	18	71	-26
	TiF ₃ ⁺⁺	-31	18	-79
Fe ⁺⁺	FeF ⁺	23 ^g	23	
	FeF ₂ ⁺⁺	59	112	15
	FeF ₃ ⁺⁺	95	144	47

^a Data from ref 17. All possible MF_n^+ products for which data are available are listed. ^b Values pertain to the gas phase reaction,



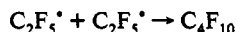
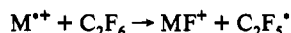
taking place in a single collision event involving a single C_2F_6 molecule.

^c Values pertain to the gas-phase reaction sequence,



in which each subsequent collision involves a different C_2F_6 molecule.

^d Values pertain to the gas-phase reaction sequence



in which C—C single bonds are formed each time a pair of C_2F_5 radicals are available. ^e Data not available. ^f Based on data from: Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 163. ^g Bauschlicher, C. W., Jr., personal communication, May 1994.

$Mo(CO)_3^{++}$ and $Mo(CO)_2^{++}$ projectiles exhibit up to two fluorine additions at 30 eV. The collision energy dependence is consistent with a reaction pathway which involves the dissociation of the projectile prior to or in concert with fluorine bond formation. In addition to the MoF_n^+ ions, the carbonyl-containing projectiles also yield fluorine abstraction products which contain a fluoro-carbon group, e.g. $MoCF_3^+$, or one or two carbonyl groups, e.g. $Mo(CO)_2F^+$. (Corresponding reactions of negative ions at a fluorinated surface have also been observed recently, e.g. $W(CO)_n^- \rightarrow WF_m(CO)_2^-, n > m$).¹⁸

A most striking example of ion/surface reactivity is that observed in the case of W^{++} . Figure 3 shows the scattered ion spectrum when a W^{++} ion beam impinges upon the fluorinated SAM surface at 30 eV collision energy. The spectrum displays the presence of products containing up to five fluorine atoms. Apart from the fluorine abstraction products WF_n^+ , the spectrum also shows the presence of carbon-containing ions WCF_n^+ in low abundance. The same reaction products are obtained with $W(CO)_6^{++}$ and $W(CO)_3^{++}$ projectile ions, which, in addition, yield carbonyl-containing fluorine abstraction products, as in the

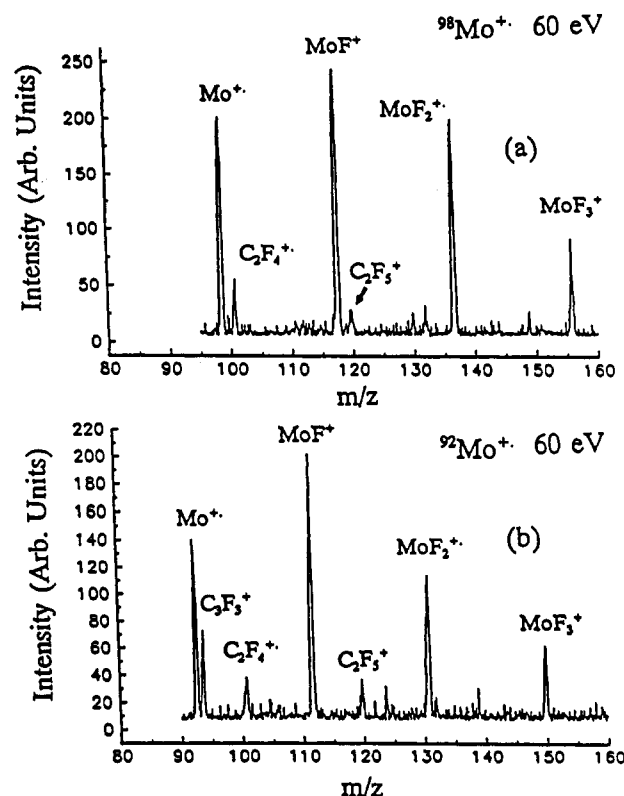


Figure 2. A portion of the scattered ion mass spectra obtained when 60 eV beams of (a) $^{98}Mo^{++}$ and (b) $^{92}Mo^{++}$ collide at the fluorinated SAM surface. Note that the metal-containing peaks are shifted by 6 amu in the two spectra.

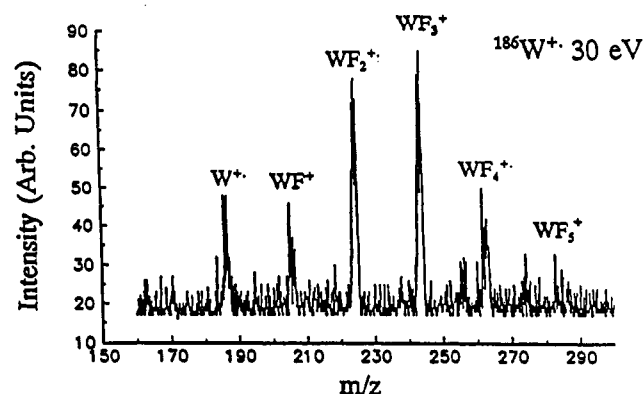


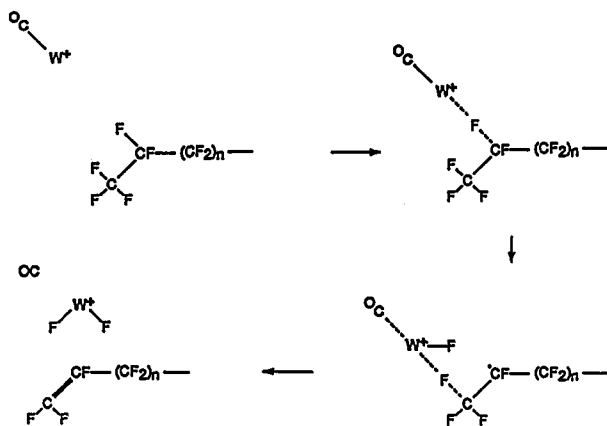
Figure 3. A portion of the scattered ion mass spectrum obtained when a 30 eV beam of $^{186}W^{++}$ collides at the fluorinated SAM surface.

case of molybdenum (Table 1). Further paralleling the behavior of molybdenum carbonylions, $W(CO)_n^{++}$ ions require more energy than W^{++} ions in order to yield WF_n^+ products, consistent with the mechanism proposed above. One of the most striking differences between the W^{++} spectrum (Figure 3) and those of other metal ions is the unexpected abundance distribution of WF_n^+ reaction products. Not only are multiple fluorine atoms abstracted, but the most abundant peaks are those for $n = 2$ and 3. In most other cases, a rapid decrease in the intensity of the MF_n^+ peaks is observed as n increases. It seems reasonable to associate the behavior of W^{++} ions with a direct abstraction process; an alternative process, in which each fluorine atom is abstracted in a separate collision, would not be expected to result in such an abundance distribution, since the probability of one projectile undergoing sequential collisions should decrease monotonically with the number of such collisions. A possible mechanism through which multiple fluorine atoms can be abstracted is exemplified

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Scheme 1



by the reaction of the $W(CO)_6^{++}$ projectile, as shown in Scheme 1. The scheme is meant to illustrate one of a number of related processes, which may differ in detail but which all involve oxidative addition at tungsten without electron transfer. Thermochemically, the multiple fluorine abstraction process in a single event is more favorable than the sequential abstractions from different fluorocarbon molecules.¹⁷ Thus, for example, the direct reaction to form WF_2^{++} from W^{++} and C_2F_6 is *exothermic* by 34 kcal/mol, while the sequential reaction, $W^{++} \rightarrow WF^+ \rightarrow WF_2^{++}$, in which two C_2F_6 molecules are involved, is *endothermic* by a total of 19 kcal/mol.

The same general considerations and type of mechanism are likely for the other metals. Note that the thermochemistry of metal fluoride formation is most favorable for W^{++} and becomes less so in the sequence $W^{++} > Mo^{++} > Ti^{++} > Fe^{++} > Cr^{++}$. The maximum number of fluorine atoms that these projectiles abstract follows the same order. In addition, the spatial extension of atomic orbitals decreases, in going from W^{++} to Cr^{++} , and this can be a reason why different distributions of MF_n^+ products are observed.

We have studied a few other ions apart from those of group VIB. Figure 4 shows the reaction product spectrum recorded when a 30 eV $^{48}Ti^{++}$ ion beam collides at the fluorinated SAM surface. Abstraction of one and two fluorine atoms is clearly seen. The third fluorine pickup is weak, but it appears in a spectrum recorded at a higher collision energy. Other fragment ions derived from $TiCl_4^{++}$ were also studied in order to investigate their tendency for fluorine atom abstraction (Table 1). Products such as $TiClF^+$ and $TiClF_2^+$ were seen, in addition to TiF_n^+ ions. As in the cases of other metal ions, polyatomic projectiles require more energy for the formation of given abstraction products than do the bare metal ions. Ions derived from $Ti(Cp)_2Cl_2^{++}$ were also investigated and gave analogous results (Table 1).

Figure 5a shows the spectrum recorded upon collisions of a 30 eV $^{56}Fe^{++}$ beam at the fluorinated SAM surface. Only single fluorine addition to the metal ion is seen. As the collision energy is increased to 60 eV, both FeF^+ and FeF_2^{++} are observed (Figure 5b). The same reaction products were seen when other Fe-containing ions such as $FeCp^+$ or $Fe(Cp)_2^{++}$ were used as projectiles. Again, in parallel with the behavior discussed above, higher collision energies were required in these cases in order to effect the corresponding ion/surface reactions. Note that in Figure 5a, no chemical sputtering products are seen, although the ion/surface reaction product (FeF^+) is observed in good abundance. If the mechanism of ion/surface reaction involved electron transfer from the surface to the projectile as the first step, creating a charged species at the surface, then provided that enough energy is transferred into the surface (which is the case for 30 eV collisions^{8,11b}) one would expect the corresponding chemical sputtering products to occur in the spectrum. Their

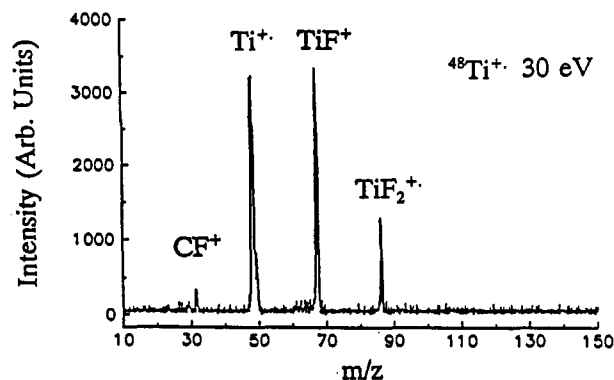


Figure 4. The scattered ion mass spectrum obtained when a 30 eV beam of $^{48}Ti^{++}$ ions collides at the fluorinated SAM surface.

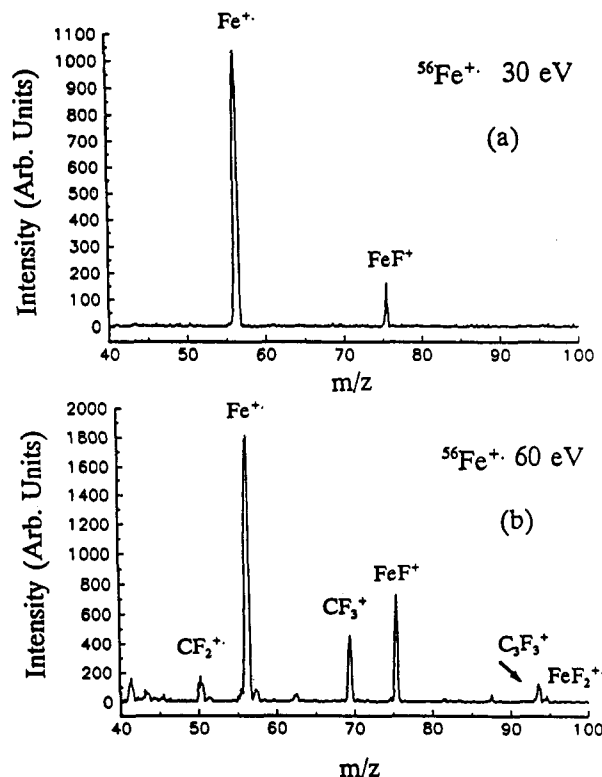


Figure 5. A portion of the scattered ion mass spectra obtained when a $^{56}Fe^{++}$ ion beam impinges upon the fluorinated SAM surface at (a) 30 eV and (b) 60 eV collision energy.

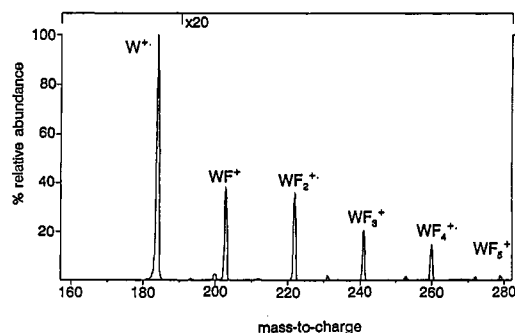
absence suggests that an alternative mechanism, not initiated by electron transfer, might be operative (cf. Scheme 1).

In an effort to further understand the ion/surface reaction process, the corresponding gas-phase ion/molecule reactions of tungsten-containing ions with perfluorohexane collision gas were examined in a triple quadrupole mass spectrometer. Each of the $W(CO)_n^{++}$ ($n = 0-6$) ions was reacted with perfluorohexane at a collision gas pressure of 0.4 mTorr and a collision energy of 10 eV. The results of this study are summarized in Table 3. In addition to the reaction products shown in this table, ions were observed corresponding to the fragmentation of the tungsten hexacarbonyl projectile, as well as to the dissociative charge exchange of perfluorohexane collision gas, yielding fluorocarbon peaks, such as m/z 69 (CF_3^+), in the product ion spectrum. The partial spectrum shown in Figure 6 demonstrates that the abstraction of 1-5 fluorine atoms occurs by the tungsten projectile. At higher collision gas pressures (e.g. 3.0 mTorr), the peaks corresponding to the tungsten reaction products become much more intense, constituting more than 10% of the total ion current.

Table 3. Ion/Molecule Reaction Products for the Reaction of Tungsten Hexacarbonyl Derived Ions with Perfluorohexane at a Pressure of 0.4 mTorr and a Collision Energy of 10 eV^a

projectile ion	product ions (% relative abundance) ^{b,c}
W	WF (100), WF ₂ (96), WF ₃ (50), WCF ₃ (4), WF ₄ (37), WCF ₄ (5), WF ₅ (4), WC ₂ F ₄ (4), WC ₂ F ₅ (10)
WCO	WF (46), WF ₂ (100), WF ₃ (45), WCF ₃ (4), WF ₄ (60), WCF ₄ (4), WF ₅ (9), WC ₂ F ₄ (4), WC ₂ F ₅ (28), W(CO)C ₆ F ₁₄ (6)
W(CO) ₂	WF (19), WF ₂ (100), W(CO)F (38), WCF ₂ (7), WF ₃ (32), W(CO)F ₂ (16), W(CO) ₂ F (6), WF ₄ (69), WCF ₄ (7), WF ₅ (17), WC ₂ F ₅ (32), W(CO)C ₆ F ₁₄ (35), W(CO) ₂ C ₆ F ₁₄ (10)
W(CO) ₃	WF ₂ (45), W(CO)F (23), WF ₃ (22), W(CO)F ₂ (100), W(CO) ₂ F (74), WF ₄ (70), W(CO)CF ₂ (10), W(CO) ₂ F ₂ (71), WF ₅ (16), W(CO) ₃ F (55), WC ₂ F ₅ (35), W(CO) ₃ C ₆ F ₁₄ (24), W(CO) ₂ C ₆ F ₁₄ (100), W(CO) ₃ C ₆ F ₁₄ (50)
W(CO) ₄	W(CO) ₃ F (50), W(CO)F ₂ (21), W(CO) ₂ F ₂ (87), W(CO) ₂ C ₆ F ₁₄ (30), W(CO) ₃ C ₆ F ₁₄ (100)
W(CO) ₅	W(CO) ₃ C ₆ F ₁₄ (100), W(CO) ₄ C ₆ F ₁₄ (34)
W(CO) ₆	W(CO) ₃ C ₆ F ₁₄ (92), W(CO) ₄ C ₆ F ₁₄ (100)

^a Only those tungsten-containing ions which incorporate fluorine atoms or fluorocarbon fragments are listed. Conditions correspond to attenuation of the projectile beam by 25%. ^b All projectiles and products are singly charged positive ions. ^c Relative abundances (given in parentheses) are with respect to the most abundant ion/molecule reaction product.

**Figure 6.** A partial product ion mass spectrum obtained upon a gas-phase reaction between the tungsten ion and perfluorohexane collision gas at 10 eV translational energy and 0.4 mTorr pressure in a triple quadrupole mass spectrometer. Note the presence of up to five fluorine atom abstractions by tungsten.

The presence of a low abundance, but significant, peak at m/z 522 should be noted; it corresponds to the attachment of an entire molecule of C₆F₁₄ to the tungsten ion. In a series of experiments involving different tungsten carbonyl projectiles, a number of such complex ions have been observed, e.g. [WO + C₆F₁₄]⁺, [W(CO) + C₆F₁₄]⁺, and [W(CO)₂ + C₆F₁₄]⁺. These observations suggest that a collision complex is formed, which can facilitate the transfer of multiple fluorine atoms from the collision gas molecule to the projectile ion. Experiments with perfluoroethane at 0.4 mTorr and 10 eV show the pickup of up to four fluorine atoms by tungsten, while the corresponding collisions with perfluoromethane yield WF_{*n*}⁺ ($n = 1-3$) products. With 0.4 mTorr of perfluorohexane in the collision quadrupole, an ion beam attenuation of 25% was measured (compared to its intensity prior to the collision gas introduction). Another experiment was performed in which the beam attenuation was reduced to 5%. The overall abundance of the fluorine addition peaks relative to the tungsten ion peak diminished, but the abstraction of up to four fluorine atoms by tungsten ion was still evident. While there may be more than one mechanism involved in gas-phase ion/molecule reactions, these results suggest that the abstraction of multiple fluorine atoms from fluorocarbon molecules by tungsten ions can occur during a *single* collision event.

The ion/surface reaction products observed upon collisions at a perfluorinated polyether (PFPE) liquid surface are almost identical to those obtained from the SAM surface at similar energies.^{4,16} The projectiles investigated were W⁺, W(CO)₆⁺,

and Cr(CO)₆⁺; W⁺ gave WF₂O⁺ (5%, relative abundance) and WF₃O⁺ (10%), in addition to the expected products WF_{*n*}⁺ ($n \leq 5$), which exhibited similar intensities as in the case of the fluorinated SAM surface (see Table 1). No oxygenated products were seen with W(CO)₆⁺ or Cr(CO)₆⁺ projectiles. In addition to the MF_{*n*}⁺ products, the carbonyl projectiles also show fluorine abstraction products that contain one or more carbonyl groups. In parallel to the behavior observed at the SAM surface, these projectiles required higher collision energies than the atomic metal ions in order to yield similar reaction products.

Helium scattering experiments from a perfluorinated acid ester monolayer²⁰ have shown that helium atoms undergo direct scattering from the terminal -CF₃ groups. The same study demonstrated that the SAM surface is microscopically ordered and that the alkyl chains form a well-ordered lattice. Similar inferences were reached by other authors employing different types of SAM surfaces.^{19,21,22} Scanning tunneling microscopy studies²³ show that the gold film used to prepare the monolayer is predominantly (111) and that the crystallites are ~3000 Å wide. The fluoroalkyl chains form a periodic hexagonal pattern, with equal nearest and next nearest neighbor distances of 5.8 and 10.1 Å, respectively.²⁴ This means that the monolayer forms a (2×2) adlayer on the Au(111) lattice. The chains appear to be fully extended and tilted by 16° from the surface normal.²⁴ It was also found that the monolayers are resistant to ion penetration²¹ in electrochemical experiments. On the basis of the findings of the above studies, it might be suggested that an ion colliding at a perfluorinated SAM surface will be most likely to undergo direct scattering from the protruding -CF₃ groups or the fluorine atoms.

In order to examine the scattering process in some more detail, we carried out angle resolved measurements with W⁺ projectile ions. Although the instrument provides precise control over the incident and scattering angles, the fact that the area sampled by the ion beam (ca. 3 mm²) is expected to be much larger than the individual regions of order, as well as possible surface defects, imposes certain limitations in evaluating the angular dependence data. These results are presented in Figure 7. In this set of experiments, the incident angle was kept constant and the scattering angle was varied successively from 90° to 70° (i.e., from specular toward more grazing). As the scattering angle becomes more grazing (spectrum c in Figure 7 corresponds to a 40° angle to the plane of the surface), the relative intensity of the WF_{*n*}⁺ peaks increases for small values of n . It can also be seen that under the more grazing scattering conditions, the number of W⁺ projectile ions leaving the surface without undergoing reaction increases. These observations suggest that single scattering events are largely responsible for the formation of WF_{*n*}⁺ ions. Were the abstraction reactions primarily due to multiple scattering events (e.g. some type of a rolling collision mechanism), WF_{*n*}⁺ products with larger n values would be expected to exhibit higher intensities at grazing scattering angles, which is not observed. As already pointed out, thermochemical considerations do not favor sequential pickup of fluorine atoms either. The above experiments, including the gas-phase data, support the notion of a single collision-multiple pickup event taking place.

Although the ion/surface collision experiments, supported by gas-phase ion/molecule reactions, suggest that direct reaction processes are largely responsible for fluorine atom pickup, they do not provide information about the time an ion spends on the surface. In the single scattering event itself, there could be a short period during which the ion is temporarily bound to the

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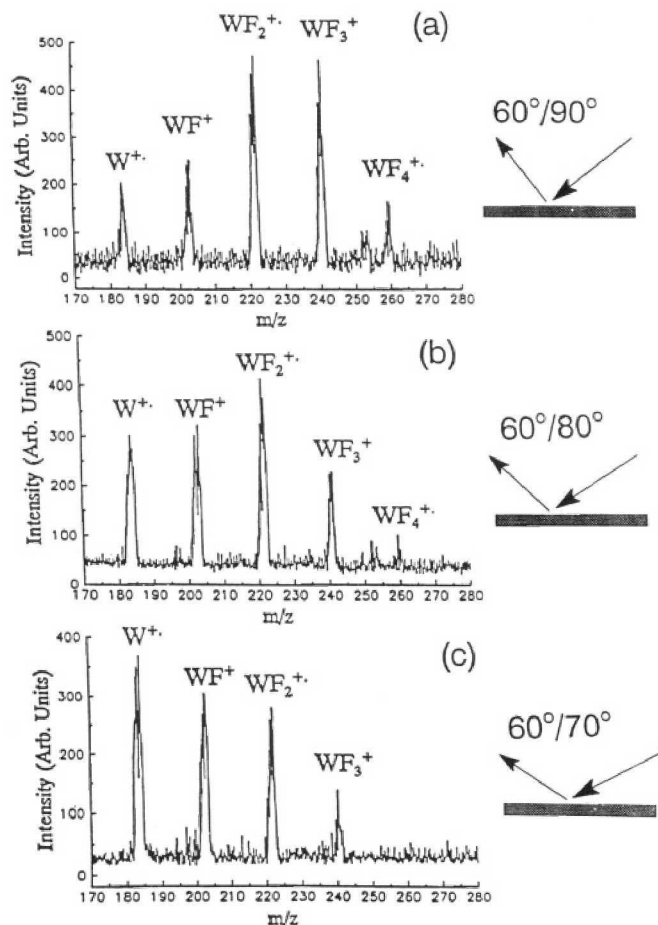


Figure 7. Partial product ion mass spectra obtained upon 30 eV collisions of $^{184}\text{W}^{++}$ at the fluorinated SAM surface at different scattering angles. The incident angle is fixed at 60° , while the scattering angle is (a) 90° , (b) 80° , and (c) 70° . Note that the intensities of the peaks at lower mass numbers increase as the scattering angle becomes more grazing. Note the absence of WF_4^+ and WF_3^+ at m/z 260 and 253 in part c.

surface. If this indeed happened, the ion would lose most of its translational energy and would be released from the surface with a very small translational energy. Preliminary measurements of the translational energy of the scattered ions seem to support the above suggestions.

At 80 eV electron impact, some projectile ions might be formed in electronically excited states in the ion source.²⁵ There are reports in the literature which show that excited state ion/molecule chemistry of transition metal ions differs substantially from that of their ground states.²⁵ Jiao and Freiser²⁶ have reported that while kinetically hot Cr^{++} reacts with SF_6 to form CrF^+ and CrF_2^+ , thermalized ions are unreactive. Ion/molecule reactions²⁷ between Cr^{++} and methane show that electronically excited ions produce predominantly CrCH_2^+ , while ground state ions produce CrH^+ . However, there is no evidence that these excited states influence the chemistry described here. In the case of 60 eV collisions of $\text{Cr}(\text{CO})_6^{++}$, $\text{Mo}(\text{CO})_6^{++}$, $\text{W}(\text{CO})_6^{++}$, and TiCl_4^{++} , as the ionizing electron energy was reduced to a nominal 16 eV (no further decrease was possible), no significant change in scattered ion spectra, including multiple fluorine abstraction products, could be observed. Since the excited states of these ions involve only s and d orbitals and optical transitions between them are partially forbidden, the excited states are long-lived and may not decay during the flight time ($\sim 100 \mu\text{s}$), but might do so near the solid

surface. Moreover, even if the projectiles colliding at the surface were in their ground state, it would still be possible that surface-induced activation and dissociation products could be formed in electronically excited states.²⁸ From the foregoing arguments, it appears that the ion/surface reactions in these cases would not be expected to differentiate between the ground state and excited states of the projectile, as our experiments indeed show.

The data of Table 1 show that the metal ions bearing ligands are less reactive than the corresponding bare metal ions; this observation remains valid even after allowance is made for the difference in their translational energies. The bare metal ions yield more abstraction products at lower collision energies compared to projectiles containing one or more ligands. It can also be seen that hexacarbonyl ions are less reactive than their tri- or dicarbonyl analogs. These observations may help answer some basic questions concerning the mechanism of ion/surface reactions. If the mechanism of product formation involved fluorine abstraction followed by dissociation of the adduct, an increase in collision energy would favor the production of lower mass ions, as a result of increased fragmentation of higher internal energy ions formed in the first step. The behavior observed points to the contrary. Consider, for example, the collisions of the $\text{W}(\text{CO})_3^{++}$ projectile at 30 and 60 eV collision energy. The increase in collision energy favors the formation of a more complex species, such as WF_3^+ , WF_4^+ , WCF_3^+ , and WCF_4^+ ions. At higher collision energy, the dissociation of the projectile yields more of the lower mass more reactive fragment ions, which are capable of abstracting a larger number of surface species. Thus, it may be concluded that ion/surface reactions predominantly occur by dissociation of the projectile, followed by (or concerted with) fluorine pickup reaction (compare Scheme 1). These observations parallel those reported recently in a study of surface collisions of CH_3I^{++} , which showed that a variety of ion/surface reaction products involve the formation of an iodine atom or ion as the first step.¹²

Unlike hydrogen atom and alkyl radical abstraction by organic projectile ions,^{5,6} the processes described above do not require ion neutralization before reaction. In the ion/surface collisions of the type studied here, the scattering takes place only from an atom or a group of atoms and the charge may remain localized. Unlike the case of organic projectiles, the ionization energy of the metal is lower than or comparable to that of the surface and so there is no energetic reason why electron transfer should occur. Note, however, that this mechanism need not apply to all fluorine abstraction ion/surface reactions; indeed, as described in the Introduction, there is evidence that electron transfer does occur in some cases,¹² including some in which organic ions undergo fluorine atom abstraction.

Conclusions

Transition metal ions undergo unusual endothermic reactions at fluorinated SAM surfaces resulting in the formation of MF_n^+ ($n \leq 5$) ions. More complex, ligated projectiles also exhibit fluorine atom abstraction. These latter ions are less reactive and require a higher collision energy than the bare metal ions in order to yield the same ion/surface reaction products. This is the first reported case of multiple bond formation with metal ions in ion/surface reactions. Similar reactions take place at other fluorine-containing surfaces, such as a liquid perfluorinated polyether.¹⁶ Angle resolved studies of these processes suggest that fluorine pickup occurs predominantly by direct ion/surface interactions involving orbitals of the projectile and those of the surface species. This mechanism is further supported by ion/molecule reactions in the gas phase, which show that tungsten hexacarbonyl derived ions undergo multiple fluorine atom addition even under single-collision conditions. Thermochemical considerations also favor

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the formation of WF_n^+ products in a single-collision event. These reactions are driven by the translational energy of the projectile ions and appear not to be preceded by electron transfer. Dissociation precedes or accompanies bond formation.

The occurrence of ion/surface reactions with high efficiency suggests that this method could be used to create reaction sites at surfaces which could subsequently be used to modify the surface chemically. One can visualize this kind of surface chemistry as a potentially important means of generating radical species at surfaces. We have begun to study the surface chemical constitution after the reaction and we expect that the radicals, created as a result of ion/surface reactions, should be available to undergo a variety of processes leading to the formation of chemically

stable products. Some of the many possibilities include polymerization involving adjacent monomers, elimination of a radical to form an unsaturated bond, and reactions with an adsorbate. If appropriate chemical species are introduced at the surface while the radicals are being formed, it should be possible to generate modified surfaces. Selective reactions could result in surfaces having novel properties. Ion/surface reactions, followed by annealing of the reactive site by an appropriate chemical species, may be a method for carrying out chemical writing.¹³

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