

# C–F and C–C Bond Activation by Transition Metals in Low Energy Atomic Ion/Surface Collisions

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**The transition metal ions,  $\text{Cr}^{+}$ ,  $\text{Mo}^{+}$ ,  $\text{W}^{+}$  and  $\text{Re}^{+}$ , abstract one or more fluorine atoms or  $\text{C}_m\text{F}_n$  groups ( $m = 1, 2$ ;  $n = 1-5$ ) in collisions with fluorocarbon self-assembled monolayers (F-SAMs). The number of atoms abstracted increases with collision energy, and with  $\text{W}^{+}$  and  $\text{Re}^{+}$  it is possible to maximize a specific scattered product ion by selecting the appropriate collision energy. The collision energy dependence suggests that dissociation of the products of multiple abstractions is not an important source of any of the observed ion/surface reaction products. The ions  $\text{W}^{+}$  and  $\text{Re}^{+}$  activate and insert into C–C as well as C–F bonds. In  $\text{Re}^{+}$  collisions, products of C–C bond activation are of comparable intensity to the C–F activation products. The reactivity of the ions towards fluorine abstraction is observed to be  $\text{Cr}^{+} < \text{Mo}^{+} < \text{W}^{+} < \text{Re}^{+}$ . The data are interpreted in terms of reaction at the surface and are rationalized by considering three factors (i) the electronic structures of the ions, (ii) the thermochemistry of fluorine abstraction, and (iii) the degree of orbital overlap of the metal ion and the F-SAM substrate. Copyright © 1999 John Wiley & Sons, Ltd.**

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The activation of the C–F bond is a topic of increasing interest, both in solution and the gas phase.<sup>1–4</sup> One method of achieving this objective is through the use of gas-phase ions, which is examined here in the case of fluorocarbon surfaces. Desorption of species from surfaces can be accomplished using keV, as well as hyperthermal ion beams. Bombardment with keV beams causes both neutrals and ions to desorb from the surface.<sup>5</sup> Interactions of hyperthermal (<100 eV) ions with surfaces bearing reactive groups can lead to the formation of new chemical bonds in the scattered ions and/or in the surface, in processes known as ion/surface (I/S) reactions.<sup>6–10</sup> These processes have been investigated for several years,<sup>6,11</sup> the principal surfaces examined being well-defined self-assembled monolayers. Of the variety of I/S reactions studied so far, hydrogen and fluorine atom abstraction reactions are the best understood.<sup>12–14</sup> A large variety of atomic and polyatomic projectile ions have been shown to abstract fluorine atoms from fluorocarbon surfaces.<sup>15–17</sup> With most projectiles, single fluorine atom abstraction is the only or the dominant process which is observed;<sup>12</sup> however, transition metal ions abstract multiple fluorine atoms. Tungsten ions, for example, pick up as many as five fluorine atoms in a single collision event.<sup>12,18</sup> Single collision events that can lead to multiple abstraction processes are also known in the case of

hydrogen atom abstractions.<sup>19</sup> Generally, atomic ions are found to be more reactive than their polyatomic counterparts in C–F bond activation. The reactions in general are thermochemically controlled, in the simple sense that those of lower energy requirement are preferred. Nevertheless, thermochemical control alone is inadequate to explain all the experimental observations,<sup>14</sup> such as the lack of multiple fluorine atom abstractions by  $\text{C}^{+}$  and its ready occurrence for  $\text{B}^{+}$  (unpublished results).

There is valuable information in the intensity distribution of the fluorine abstraction products. When using  $\text{W}^{+}$  as the projectile ions at an appropriate collision energy, the mass spectrum forms a roughly Gaussian distribution with  $\text{WF}_2^{+}$  and  $\text{WF}_3^{+}$  as the most intense peaks.<sup>12</sup> The intensity distribution changes substantially when the angle of incidence of the primary beam is varied.<sup>12</sup> Products with fewer fluorine atoms are enhanced by increasing the angle of incidence. It is of interest to see how the distribution changes with collision energy, since an evaluation of the collision energy dependence data and comparison with the corresponding gas-phase data might provide additional information on the reaction mechanism, including whether the reaction occurs at the surface, as assumed in previous studies, or above the surface.

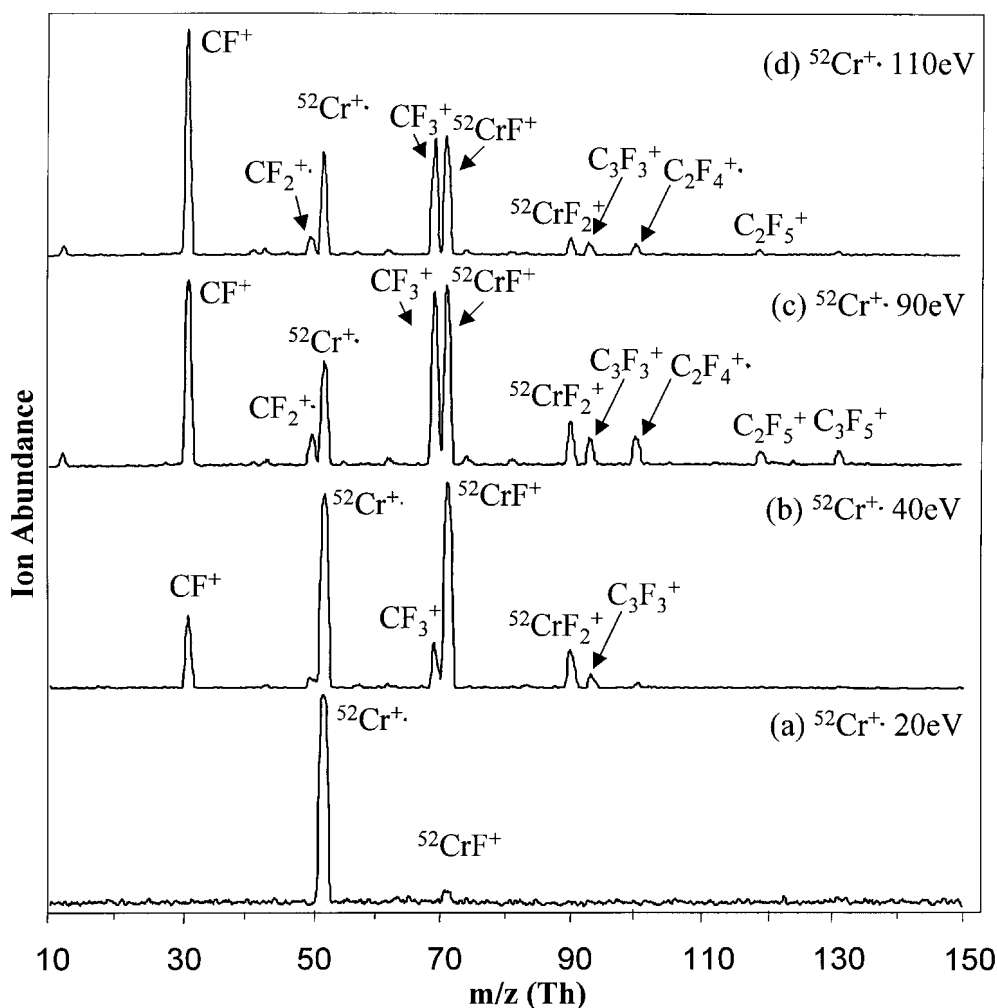
The latter possibility is considered because of the recent proposal that in some specific cases, ion/surface reactions are due to collision-induced desorption of an adsorbate followed by ion/molecule reactions in the gas phase.<sup>20–22</sup> Recent observations on specific ion/surface reactions show that the product distributions reflect the adsorption geometry of the species at the surface, and cannot be explained if the processes occur in the gas phase (unpublished results). Nevertheless, it is of interest to see whether there is

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**Figure 1.** Scattered ion mass spectra recorded upon collision of  $^{52}\text{Cr}^+$  at a fluorocarbon monolayer surface at various incident energies. The collision energies and the ion/surface reaction products are indicated.

additional evidence on the location of the bond-forming interaction from collision energy dependent studies of fluorine atom abstraction.

With this objective in view, we conducted a study of the collision energy dependence of the fluorine abstraction reactions of the transition metal ions,  $\text{Cr}^+$ ,  $\text{Mo}^+$ ,  $\text{W}^+$ , and  $\text{Re}^+$ . The results show that single atom abstraction is most facile at low collision energies and as the collision energy increases, the product intensity shifts towards multiple fluorine abstraction. It is possible to maximize the abundance of any of the  $\text{W}^+$  or  $\text{Re}^+$  product ions by appropriate selection of energy at a given incident angle.

## EXPERIMENTAL

The ion/surface scattering experiments were conducted using a four-analyzer BEEQ mass spectrometer described previously.<sup>23</sup> A mass- and energy- analyzed ion beam is directed at the surface held in an ultra-high vacuum scattering chamber, and decelerated to the desired energy prior to collision with the fluorinated self-assembled monolayer surface. The energy and mass distribution of the product ions is analyzed using the remaining EQ analyzers. In the experiments described below, the angle of incidence was  $55^\circ$  relative to the surface normal and the scattering angle relative to the incident beam was set at  $90^\circ$ ,

although this parameter could be varied. The experiments were conducted at a base pressure of  $5 \times 10^{-9}$  Torr, which was not changed on introduction of the sample into the ion source. All data are recorded in Thomson, where 1 Th = 1 Dalton/electronic charge.<sup>24</sup> The collision energy range investigated in these experiments was 10–200 eV. Primary ions were generated by 70 eV electron impact upon  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$  and  $\text{Re}_2(\text{CO})_{10}$  (Aldrich Chemical Co., Milwaukee, WI, USA) and  $\text{C}_6\text{F}_{14}$  (Lancaster, Windham, NH, USA).

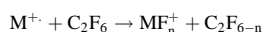
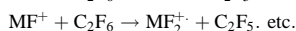
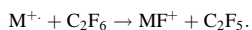
The target surface, a fluorocarbon self-assembled monolayer,  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{S-Au}$ , was prepared<sup>25,26</sup> by exposing a 1 mM solution of the corresponding thiol solution in ethanol to a clean gold surface for at least 24 hours. After self-assembly, the monolayer surface was sonicated in ethanol for a minute and washed repeatedly in ethanol and hexane, then dried under a stream of nitrogen. The gold surface was prepared by thermal evaporation of Au (2000 Å) on a (111) polished Si crystal face (with sputter-deposited 5 nm buffer layer of Cr). X-ray diffraction of the gold surface prepared in this way showed (111) reflections (Siemens diffractometer).

## RESULTS AND DISCUSSION

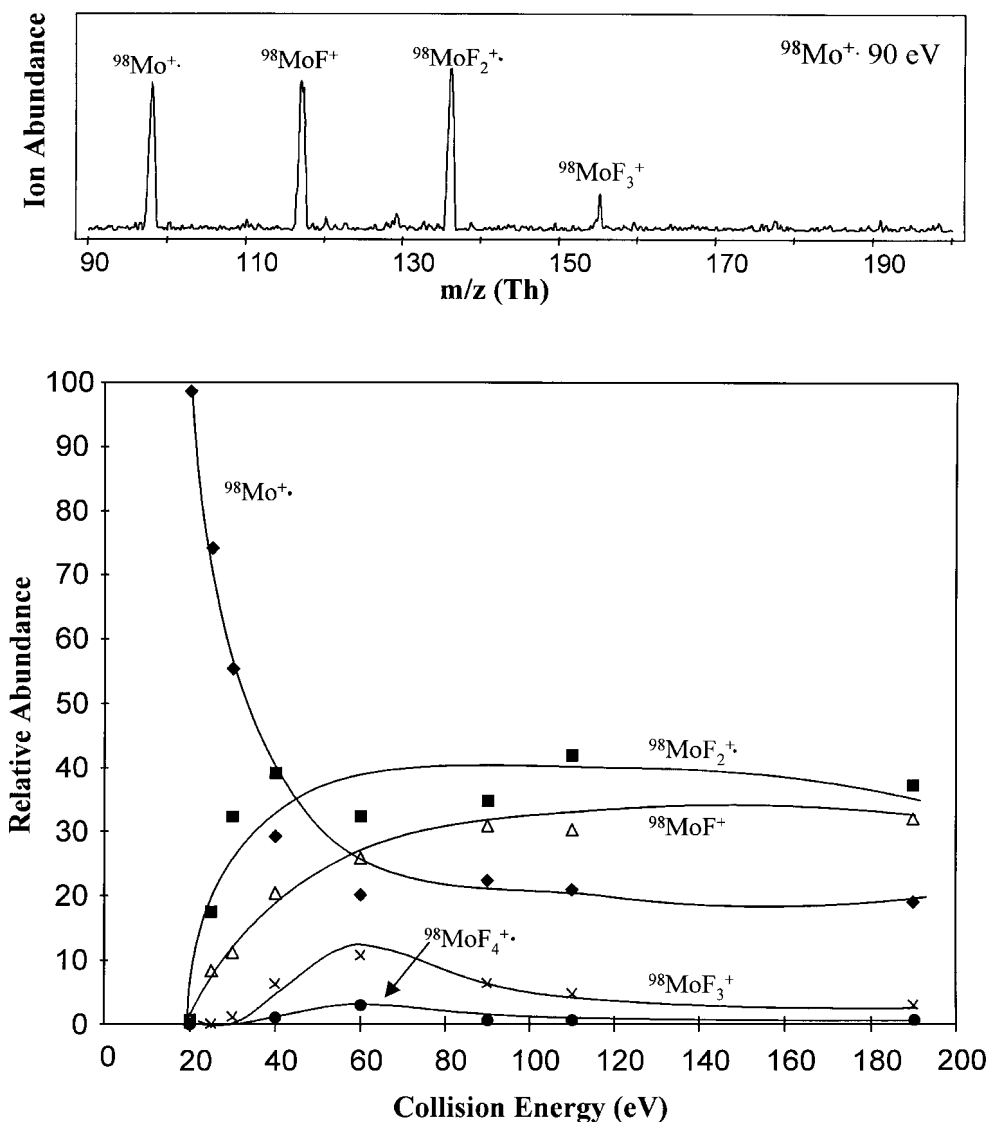
Figure 1 shows the scattered ion mass spectra recorded upon

**Table 1. Thermochemical data for formation of  $\text{MF}_n^+$  products from gas-phase reactions of  $\text{Cr}^{+\cdot}$  and  $\text{Mo}^{+\cdot}$  with  $\text{C}_2\text{F}_6^a$** 

Projectile	Product	Heat of reaction, kcal/mol	
		C=C bond formation (when applicable) <sup>b</sup>	no C=C bond formation <sup>c</sup>
$\text{Cr}^{+\cdot}$	$\text{CrF}^+$	56	56
	$\text{CrF}_2^+$	93	146
	$\text{CrF}_3^+$	148	197
$\text{Mo}^{+\cdot}$	$\text{MoF}^+$	36	36
	$\text{MoF}_2^+$	9	62
	$\text{MoF}_3^+$	41	90
	$\text{MoF}_4^+$	5	121
	$\text{MoF}_5^+$	126	175

<sup>a</sup> Data from reference 27.<sup>b</sup> Calculated from the gas-phase reaction<sup>c</sup> Calculated from the gas-phase reaction

collision of  $^{52}\text{Cr}^{+\cdot}$  at a fluorocarbon monolayer at different collision energies. The spectra include the fluorine abstraction products,  $\text{CrF}^+$  and  $\text{CrF}_2^+$ , as well as fluorocarbon ions which are characteristic products of chemical sputtering from a fluorocarbon SAM surface. Note that  $\text{CrF}^+$  is observed even at a collision energy as low as 20 eV. Note also that at this collision energy the spectrum does not show any peaks due to chemical sputtering (i.e. to the dissociative charge exchange process that yields the SAM fragments,  $\text{CF}^+$ ,  $\text{CF}_3^+$ , etc.). These peaks only appear in the mass spectrum recorded above 30 eV collision energy. This is consistent with the low recombination energy of 6.76 eV for  $\text{Cr}^+$ ,<sup>27</sup> which therefore makes fluorocarbon ion formation substantially endothermic. Referring to Fig. 1(b), note the occurrence of  $\text{C}_3\text{F}_3^+$  which is a high-energy species and is normally of lower abundance than  $\text{C}_2\text{F}_5^+$  in the  $\text{Xe}^{+\cdot}$  chemical sputtering spectrum of fluorocarbon surfaces (the threshold energies of  $\text{C}_2\text{F}_5^+$  and  $\text{C}_3\text{F}_3^+$  in  $\text{Xe}^{+\cdot}$  chemical sputtering are about 18 and 40 eV, respectively)<sup>13</sup>. Note that no  $\text{C}_2\text{F}_5^+$  is observed in Fig. 1(b). The formation of the  $\text{C}_3\text{F}_3^+$  in this spectrum is therefore believed to occur



**Figure 2.** The top panel displays the scattered ion mass spectra (90 Th and above) at 90 eV. The bottom panel displays an energy resolved mass spectrum (ERMS) plot for the ion/surface reaction products produced upon collision of  $^{98}\text{Mo}^{+\cdot}$  at a fluorocarbon monolayer surface in a collision energy range from 20 to 200 eV.

through a low-energy ion/surface reaction, in which the metal ion causes C–C cleavage and simultaneous F<sub>2</sub> elimination. The lack of an observable change in the intensity of this ion after extended Xe<sup>+</sup> chemical sputtering or surface atom/group abstraction experiments demonstrates that it is the result of a single ion/surface collision event.

Formation of CrF<sup>+</sup> in the gas phase from ground state Cr<sup>+</sup> and a typical fluorocarbon is 56 kcal/mol endothermic.<sup>27</sup> The fact that this ion displays a threshold of approximately 20 eV in ion/surface collisions (Fig. 1(a)) suggests that the surface collision converts the required 56 kcal/mol (2.4 eV, i.e. 12%) of translational into internal energy. This energy deposition in the course of charge exchange at a surface can be compared with that deposited into the scattered ion in inelastic surface collisions. In the latter case, the most probable T → V conversion efficiency is approximately 20%.<sup>28,29</sup>

The double fluorine abstraction product, CrF<sub>2</sub><sup>+</sup>, is formed at higher collision energy. This is in accordance with thermochemical considerations, since this reaction is more endothermic than single fluorine abstraction. However, even after increasing the collision energy beyond 100 eV, no CrF<sub>3</sub><sup>+</sup> is observed. The reaction thermochemical data for the formation of CrF<sub>x</sub><sup>+</sup> (x = 1–3) have been estimated<sup>27</sup> and are displayed in Table 1. As one can see, the formation of CrF<sub>3</sub><sup>+</sup> is highly endothermic, and this result emphasizes the control of thermochemistry over ion/surface reactions.

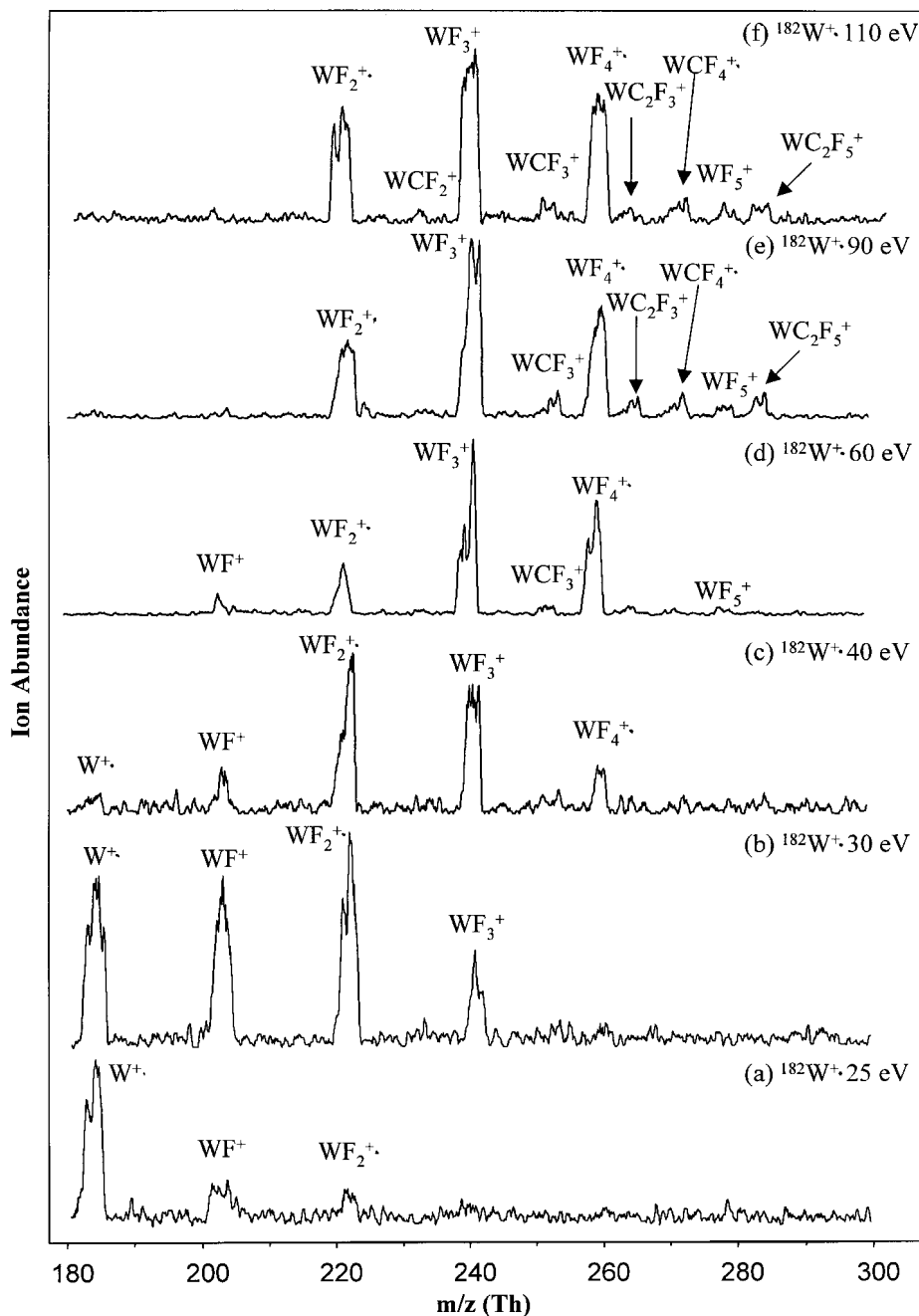
Figure 2 shows the scattered ion mass spectra recorded upon collision of <sup>98</sup>Mo<sup>+</sup> at the fluorocarbon SAM at 90 eV collision energy, as well as an energy resolved mass spectrum (ERMS) plot for collision energies ranging from 20 to 190 eV. Referring to the ERMS plot, at 20 eV collision energy, no reaction products are observable, only the projectile ion is seen. The product MoF<sup>+</sup> begins to appear in the mass spectrum at a collision energy between 20 and 25 eV. As shown in Table 1, the formation of this ion is 36 kcal/mol endothermic, 20 kcal/mol less than CrF<sup>+</sup> formation. However, the threshold collision energy for formation of CrF<sup>+</sup> was observed to be lower than the threshold energy for MoF<sup>+</sup>, 20 and 24 eV, respectively. This stresses the contribution of factors other than thermochemistry in controlling these reactive collisions. The thermochemical requirements for subsequent fluorine abstractions were estimated<sup>27</sup> and these data are also shown in Table 1. Upon increasing the collision energy to 30 eV, both MoF<sub>2</sub><sup>+</sup> and MoF<sub>3</sub><sup>+</sup> are observed, and on increasing the collision energy by an additional 10 eV, the product of four fluorine abstraction is observable. The relative abundances of the abstraction products MoF<sup>+</sup> and MoF<sub>2</sub><sup>+</sup> increase rapidly at lower energy but above 60 eV collision energy their intensities level out. At this point, and for the remainder of the collision energy range examined MoF<sub>2</sub><sup>+</sup> is the base peak. This is consistent with the small endothermicity of MoF<sub>2</sub><sup>+</sup> formation (with accompanying C=C double-bond formation). Although not shown in the ERMS plot, sputtering products are observable from 40 eV onwards. Again referring to Fig. 2, it is also of interest to see that the fractional conversion of Mo<sup>+</sup> to products (defined as Σ abundance of MoF<sub>n</sub><sup>+</sup>/abundance of incident Mo<sup>+</sup>) remains approximately constant as the collision energy increases. The fact that a maximum of only four fluorine atoms are abstracted rather than more, suggests that thermochemical factors inhibit the abstraction of more than four atoms.

Figure 3 shows the scattered ion mass spectra recorded upon collision of <sup>184</sup>W<sup>+</sup> at the fluorocarbon surface. It is interesting to see that the product ion distribution changes substantially towards higher abstraction products with an increase in collision energy. It is possible to make any ion, from WF<sup>+</sup> to WF<sub>3</sub><sup>+</sup>, the major product of the reaction, just by adjusting the collision energy. The absence of a substantial amount of W<sup>+</sup> and WF<sup>+</sup> beyond 40 eV suggests that (i) there is no substantial fragmentation of the ion/surface reaction products and (ii) that these reactions do not occur as a result of association processes in the gas phase. In the gas phase<sup>30</sup> WF<sup>+</sup> is the major reaction peak under single- and multiple-collision conditions with fluorocarbons. If there were substantial fragmentation of ion/surface reaction products at high collision energy, one would expect a reversal in the intensity pattern. However, it has to be remembered that the fragmentation products can undergo further abstraction and the co-occurrence of both fragmentation and reaction cannot be ruled out.

As the collision energy is increased, additional processes involving C–C bond cleavage and abstraction of C<sub>m</sub>F<sub>n</sub> (m = 1,2; n = 1–3) groups occur. Although the nature of the bonding in these ions is in question, it is certain that more channels of interaction become available as the collision energy is increased. Molecular dynamics studies of ion/surface interactions show that as the collision energy increases, the ion is within the interaction region of the surface for a longer period of time.<sup>31</sup> This is especially true of an organic monolayer matrix, which is expected to have a high compressibility. During such an interaction, a larger volume of the matrix is accessible to the ion.

Figure 4 presents the scattered ion mass spectrum recorded upon collision of <sup>187</sup>Re<sup>+</sup> with the fluorocarbon SAM. Many features are similar to the W<sup>+</sup> data, but the fluorocarbon abstraction products, ReCF<sup>+</sup>, ReCF<sub>2</sub><sup>+</sup> and ReCF<sub>3</sub><sup>+</sup> are now of comparable abundance to the fluorine abstraction products. It is apparent that high collision energy favors Re–C bond formation over Re–F formation. While the W<sup>+</sup> fluorocarbon abstraction products are first observed at 60 eV, the first carbonaceous abstraction product, ReCF<sub>2</sub><sup>+</sup>, is observed at only 40 eV. It is important to note that fluorocarbon abstraction products are not observed when using Cr<sup>+</sup> or Mo<sup>+</sup> as the projectile. Unfortunately, there are no bond energy values available in the literature to allow these comparisons to be taken further. However the C–C cleavage with new bond formation to the metal center can hardly be a higher energy process than the C–F cleavage process. The difference in threshold energy is therefore ascribed to the fact that the C–F bonds are at the surface, while the C–C bonds are not.

It is worth noting that the relative abundances of ReCF<sub>n</sub><sup>+</sup> (n = 1–4) do not correlate to those of the chemical sputtering products. Typical Xe<sup>+</sup> chemical sputtering spectra of fluorocarbon SAMs show an intensity of CF<sub>n</sub><sup>+</sup> peaks in the order CF<sub>3</sub><sup>+</sup> > CF<sup>+</sup> > CF<sub>2</sub><sup>+</sup>. However, ReCF<sub>2</sub><sup>+</sup> and ReCF<sub>3</sub><sup>+</sup> are roughly of the same intensity above 50 eV. Moreover, we also see peaks corresponding to ReCF<sub>4</sub><sup>+</sup>, ReC<sub>2</sub>F<sub>3</sub><sup>+</sup> and ReC<sub>2</sub>F<sub>4</sub><sup>+</sup> in the mass spectra above 50 eV, and these intensities are not inconsistent with the intensities of the fluorocarbon ions while CF<sub>4</sub><sup>+</sup> is not even observed as a chemical sputtering product. These results are all consistent with the suggestion that the reaction occurs at rather than above the surface, and that it does not involve charge exchange. Instead, mechanisms such as the fluoronium ion



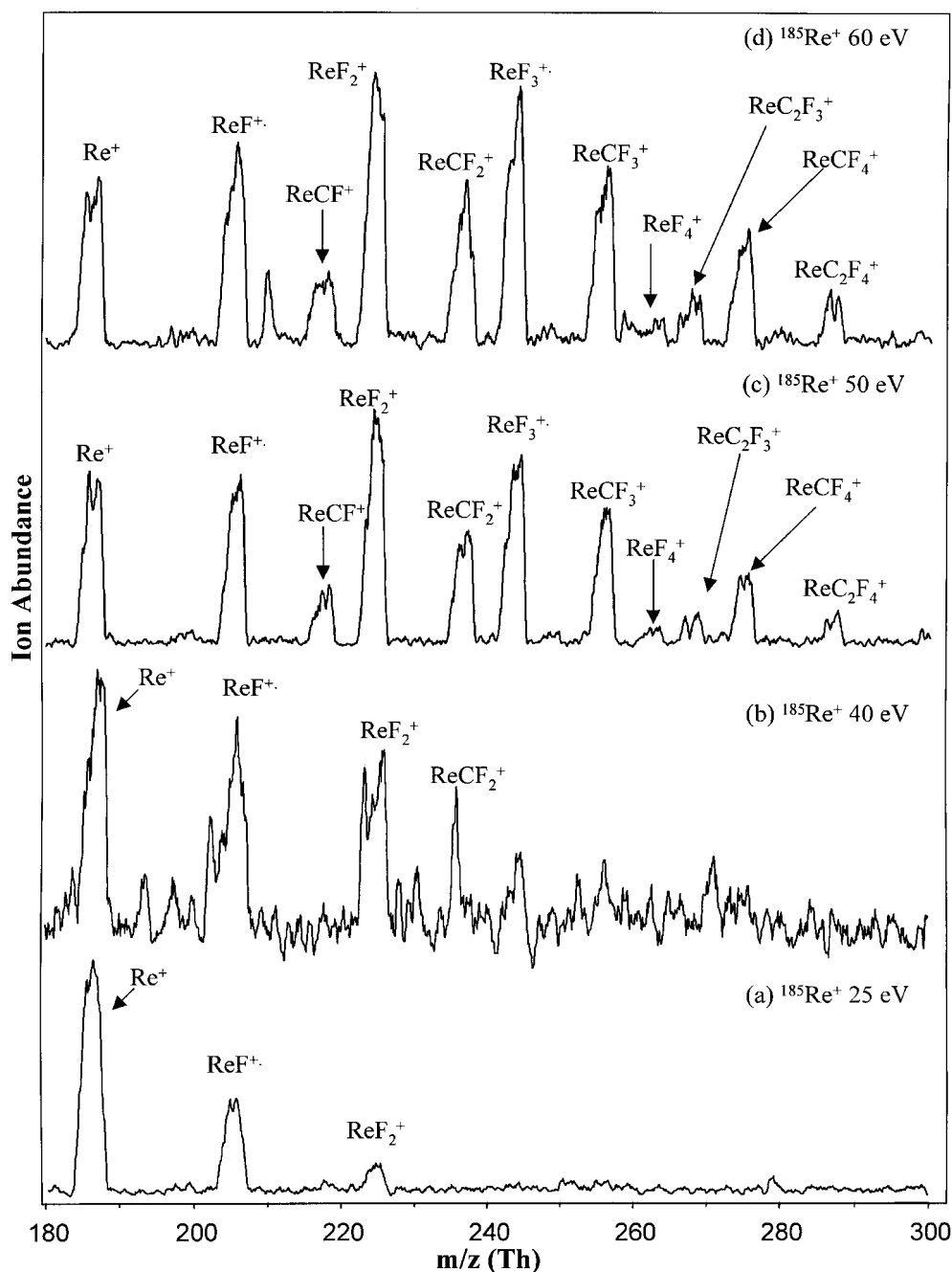
**Figure 3.** Scattered ion mass spectra (180 Th and above) recorded upon collision of  $^{182}\text{W}^+$  at a fluorocarbon monolayer surface at various incident energies. The collision energies and the ion/surface reaction products are indicated.

mechanism and C–F insertion mechanism, recently proposed in the case of  $\text{Xe}^+$  reactive scattering<sup>13</sup> are indicated.

Focusing on the differences between the scattered ion mass spectra for the different projectiles, it becomes apparent that C–C bond activation (excluding chemical sputtering peaks in the form of  $\text{C}_x\text{F}_y^+$ ) are only observed with  $\text{W}^+$  and  $\text{Re}^+$  as projectiles. This suggests that of the four projectiles ions investigated only  $\text{W}^+$  and  $\text{Re}^+$  are capable of inserting into and breaking C–C bonds. Examining these spectra even more closely, we see that the intensity of the C–C bond activation products in the  $\text{Re}^+$  spectra at high collision energies rival the intensity of the C–F bond activation products. While C–C bond activation is

observed with  $\text{W}^+$  as the projectile, it does not occur to the same extent.

Why should these transition metal ions undergo multiple fluorine abstraction reactions? Comparison with the chemistry of p-block elements studied previously<sup>32</sup> suggests that the electronic structure of the ion is important in determining the nature of the reaction product. We suggest that the electronic structure should be such that unpaired electrons must be available for an ion to undergo atom abstraction in the ion/surface collision event. Although the collision energy may be used to circumvent the activation barrier, the electronic structure has to be favorable. When both these factors are favorable, a third factor, the extent of spatial



**Figure 4.** Scattered ion mass spectra (180 Th and above) recorded upon collision of  $^{187}\text{Re}^+$  at a fluorocarbon monolayer surface at various incident energies. Due to low primary ion current, the 35 eV spectrum is noisy. The collision energies and the ion/surface reaction products are indicated.

overlap between the interacting systems, might be important in determining the number of atoms abstracted. To illustrate the point, consider the cases of  $\text{C}^{+\cdot}$  and  $\text{Tl}^{+\cdot}$ . For  $\text{C}^{+\cdot}$  ( $2s^2 2p^1$ ), although multiple fluorine abstractions are thermochemically favored, they are electronically unfavorable since C possesses only one unpaired electron. Experimental results show the abstraction of only one fluorine atom.<sup>12</sup> In the case of  $\text{Tl}^{+\cdot}$  ( $5d^{10} 6s^2$ ) neither the thermochemistry nor electronic structure (no unpaired electrons) is favorable and consequently fluorine abstraction is not observed.<sup>32</sup>

In order to illustrate these factors in the cases of the transition metal ions studied here, consider their electronic structures more closely.<sup>33</sup> The ions  $\text{Cr}^{+\cdot}$  ( $3s^2 3p^6 3d^5$ ) and  $\text{Mo}^{+\cdot}$  ( $4s^2 4p^6 4d^5$ ) both exist in  $^6\text{S}_{5/2}$  electronic ground

states, while  $\text{W}^{+\cdot}$  ( $5s^2 5p^6 5d^4 6s^1$ ) and  $\text{Re}^+$  ( $5s^2 5p^6 5d^5 6s^1$ ) have electronic ground states,  $^5\text{D}_0$  and  $^6\text{S}_{5/2}$ , respectively. The ionization energies of Cr (6.76 eV) and Mo (7.10 eV) are higher than that of W (7.98 eV) which is close to that of Re (7.87 eV). In both  $\text{Cr}^{+\cdot}$  and  $\text{Mo}^{+\cdot}$  the first excited state lies 1.47 eV higher than the ground state. In the case of  $\text{W}^{+\cdot}$ , the lowest excited state has a configuration,  $5d^5$  ( $^6\text{S}_{5/2}$ ), and is only 0.92 eV higher in energy while  $\text{Re}^+$  has a closed S-shell lowest excited state ( $5d^4 6s^2$  ( $^5\text{D}_0$ )) which is 1.71 eV higher in energy. This electronic picture suggests that all of these transition metals can undergo multiple abstraction reactions – up to five (for  $\text{W}^{+\cdot}$ ,  $\text{Mo}^{+\cdot}$  and  $\text{Cr}^{+\cdot}$ ) or six (for  $\text{Re}^+$ ) – if thermochemistry and other aspects are favorable.

Although a theoretical maximum of five or six fluorine

atoms can be abstracted, fewer abstractions are observed for  $\text{Cr}^+$ ,  $\text{Mo}^+$  and  $\text{Re}^+$ , even at high collision energies. This is most likely due to the spatial extension of the orbitals concerned. The d-orbital occupancy and dimensions of  $\text{W}^+$  and  $\text{Re}^+$  are similar. Although thermochemical values for Re-fluorides are not available, one assumes that they are similar to those of W. Since excitation energies are not high, involvement of the excited states in the reactivity cannot be ruled out for  $\text{Cr}^+$ ,  $\text{Mo}^+$  and  $\text{Re}^+$ , and they are even more likely to participate in the case of  $\text{W}^+$ . The bond energy values for the various metal-fluoride bonds are in the order,  $\text{W-F}$  (130.9 kcal/mol) >  $\text{Mo-F}$  (111.0 kcal/mol) >  $\text{Cr-F}$  (106.2 kcal/mol).

The results presented above suggest that ion/surface reactions occur at the surface, on a short time-scale. No metal ions are observed in the subsequent chemical sputtering event, suggesting that reactions occur in the course of single scattering events. The fact that it is possible to completely avoid certain products just by varying collision energy further supports the argument that all of the reaction products are formed in single ion/surface collision encounters. Had there been association reactions between the ions and the neutrals in the gas phase there would be no reason why certain products would not be produced. In fact, in the gas-phase collision experiments, the product pattern remains largely the same over a range of collision energies.<sup>34</sup> If I/S reactions occur as a result of gaseous association processes, for one to explain the absence of certain reaction products it is necessary to argue that the ions undergo multiple collisions and that reaction products undergo subsequent reactive collisions. This does not seem likely in the small interaction region within 5 Å of the surface. Particularly noteworthy is that  $\text{Re}^+$  at low collision energies produces a great deal more C–C activation and cleavage products than  $\text{W}^+$  does, while both metals have approximately the same mass. With a ground state configuration  $5s^2 5p^6 5d^5 6s^1$ ,  $\text{Re}^+$  has a large number of unpaired electrons which is surely a factor in its ability to cleave C–C bonds more readily than  $\text{W}^+$ . Thus, in order to accurately predict abstraction reactions, one must consider three factors; the electronic structure of the ions, the thermochemistry of the reaction, and finally the degree of orbital overlap between the projectile and the surface species.

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