# Low-energy Collisions of Methane Ions at a Fluoroalkyl Monolayer Surface

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Reactive scattering of low-energy (<100 eV)  $CH_n^+$  (n = 0-4) ions with a fluorinated self-assembled monolayer (F-SAM) surface produces fluorine-containing scattered ions, including  $CF^+$ ,  $C_2HF_2^+$  and  $C_3F_3^+$ . Evidence is provided that these ion-surface reactions occur by surface-induced dissociation (SID) prior to new bond formation. Chemical sputtering of the ion-beam modified surface is consistent with the modification of the fluorinated SAM surface by the methane derived ions occurring at the terminal  $CF_3$  group. Studies with <sup>13</sup>C-labeled ions show the formation of  $^{12}CF^+$  and  $^{13}CF^+$  in nearly equal abundance. The participation of carbon atoms arising from both the surface and the projectile suggests the intermediacy of a symmetrical fluoronium collision complex, such as  $[F^{13}CF^{12}CF]^+$ , involving the SID fragments of the projectile and the terminal  $CF_3$  group of the surface. A 20% translational to vibrational (T  $\rightarrow$  V) energy conversion is estimated from the inelastic collisions which lead to SID, a result which is consistent with previous studies using other ions on the same surface.

# INTRODUCTION

Although initial attempts to utilize ion-surface collisions as a means of activating gaseous ions date back to 1975,<sup>1,2</sup> the first significant breakthrough in this respect was made 10 years later, when Mabud et al.<sup>3</sup> demonstrated that low translational energy ions can be efficiently fragmented following collisions at solid surfaces. During the ensuing decade, studies of ion-surface interactions have steadily grown in both number and scope; these developments have been summarized in recent reviews.<sup>4-7</sup>

A variety of phenomena that take place upon ionsurface encounters have been identified and studied. If an incoming projectile ion is denoted by  $AB^+$ , and a surface molecule as SX (where X represents a terminal atom or functional group), then some of the main processes can be defined as follows:

Elastic scattering:

$$AB^{+} + SX \rightarrow AB^{+} + SX \tag{1}$$

Neutralization:

$$AB^+ + SX \rightarrow AB + SX^+$$
 (2)

$$AB^{+} + SX \rightarrow A + B + SX^{+}$$
(3)

Surface-induced dissociation (SID):

$$AB^+ + SX \rightarrow A^+ + B + SX$$
 (4)

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CCC 1076-5174/96/070791-11 © 1996 by John Wiley & Sons, Ltd. Ion-surface reactions:

$$AB^{+} + SX \rightarrow ABX^{+} + S \tag{5a}$$

$$\rightarrow AX^{+} + B \tag{5b}$$

Chemical sputtering:

$$AB^+ + SX \rightarrow AB + SX^+$$
 (6a)

$$\rightarrow$$
 S + X<sup>+</sup> (6b)

Apart from neutralization, which is usually an unwanted outcome of an ion-surface collision, surfaceinduced dissociation (SID) was the first phenomenon observed and studied; these inelastic collisions, that lead to fragmentation of the projectile, are an analog of collision-induced dissociation (CID) in the gas phase. Some of the properties of SID make it an attractive alternative to CID, in particular the large internal energy deposition, which is easily controllable and which exhibits a narrow distribution.<sup>8-12</sup> In that respect, SID is a promising method for activation and fragmentation of very stable or very large molecules, as has been already demonstrated for compounds such as polynuclear aromatic hydrocarbons (PAHs),<sup>13,14</sup> fullerenes,<sup>15-17</sup> disaccharides,<sup>18</sup> nucleosides<sup>19</sup> and peptides.<sup>20-24</sup>

Early experiments have revealed that another commonly occurring phenomenon is the occurrence of ionsurface reactions.<sup>25</sup> In collisions with metal targets, some ions (especially aromatic and heteroaromatic molecular ions) have been shown to pick up one or more hydrogen atoms or hydrocarbon groups, originating from adsorbates on the metal surfaces.<sup>26</sup> Use of selfassembled monolayer (SAM) surfaces as targets was an important development in SID since it minimized the degree of accompanying neutralization in ionsurface reactions:<sup>27,28</sup> by choosing the terminal functionality on the SAM chain, a different atom or group of atoms can be presented to the incoming ion. Thus, for example, fluorinated hydrocarbon SAM surfaces

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have been shown to exhibit some remarkable properties: in addition to exhibiting even less neutralization than hydrocarbon-covered surfaces, they are more effective in translational to internal energy conversion and they afford a variety of ion-surface reactions in which appropriate projectile ions pick up one or more fluorine atoms.<sup>11,29,30</sup> While polyatomic ions which react at all mainly abstract a single F atom from the surface, atomic ions (A<sup>+</sup>) exhibit a diverse behavior and AF<sub>n</sub><sup>+</sup> ions (n = 1-5) have been observed.<sup>31,32</sup> Formation of WF<sub>5</sub><sup>+</sup> is of special interest, since evidence has been provided that all five W—F bonds are formed in a single collision event.<sup>33,34</sup> Unusual species, such as XeF<sup>+</sup>, IF<sup>+</sup> and IF<sub>2</sub><sup>+</sup>, have been reported as products of reactive collisions, pointing to the unique and rich ion chemistry at surfaces.<sup>29</sup>

In many systems, the great majority of the incoming projectiles undergo neutralization at the surface. In this way, sites bearing positive charges can be temporarily created at the surface (reaction (6a)). If enough internal energy is made available, some bonds may be cleaved, and surface or adsorbate ionic fragments may be released into the gas phase (reaction (6b)). This process is referred to as chemical sputtering\* and it takes place at very low ion translational energies (eV range), in contrast to high-energy (keV) momentum transfer sputtering (physical sputtering), characteristic of secondary ion mass spectrometry. For a given target, chemical sputtering will depend on the collision energy and nature of the projectile (e.g. its mass and ionization energy). In spite of this, some common features characterize a sputtering pattern for a particular surface. Thus, metal surfaces bearing hydrocarbon adsorbates exhibit sputtering peaks corresponding to  $CH_3^+$ ,  $C_2H_3^+$ ,  $C_3H_3^+$ ,  $C_3H_5^+$ ,  $C_3H_7^+$ ,  $C_4H_7^+$ ,  $C_4H_9^+$ , etc.<sup>38</sup> The same peaks are observed for hydrocarbon SAM surfaces.<sup>28,39</sup> Fluorinated SAM surfaces also generate a characteristic series of chemical sputtering ions:  $CF^+$ ,  $CF_2^+$ ,  $CF_3^+$ ,  $C_2F_4^+$ ,  $C_2F_5^+$  and  $C_3F_5^+$ .<sup>19</sup> The presence of a new species in the sputtered ion mass spectrum can indicate that surface modification had taken place. For example, subsequent to the bombardment of a fluorinated SAM surface with  $SiCl_3^+$  projectiles, sputtering with 60 eV Xe<sup>++</sup> ions results in the observation of a  $CF_2Cl^+$  peak, pointing to the occurrence of the ion-surface transhalogenation process.40

Another point pertinent to this study concerns the actual sequence of processes in reactive collisions of a polyatomic projectile  $AB^+$  with a surface SX. In principle, three possible reaction sequences can be visual-

ized. In the first, represented by the processes (5a) and (5b), the reaction of the intact projectile represents the initial step; this is followed by subsequent fragmentation of the adduct to give a variety of product ions. Alternatively, the projectile may dissociate upon impact at the surface (e.g. as shown by reaction (4)), and the resulting nascent products may then undergo reaction with the surface. A third possibility involves neutralization of the projectile prior to its dissociation and the reaction with the surface; distinguishing between the various sequences of events may be difficult.

In order to try to elucidate ion-surface collision processes further, it was decided to investigate the behavior of a simple compound,  $CH_4$ , in terms of collisions at a fluorinated SAM surface. It was hoped that this simple system would produce a better understanding of the relationship between SID, chemical sputtering and ionsurface reactions. The availability of  $^{13}CH_4$  and  $CD_4$ labeled compounds offered the possibility to distinguish between ions due to the scattered projectile (or its fragments) and those sputtered from the surface. A series of experiments was carried out with a view to addressing the following questions: (i) how do each of the processes depend on collision energy?; (ii) what are the thresholds for each type of process and how do they relate to each other?; (iii) how do the reactivities of various methane-derived ions compare?; (iv) how do the experimental results compare with thermochemical predictions?; and (v) what conclusions can be drawn with regard to various mechanisms?

## EXPERIMENTAL

Experiments were performed using a custom-built hybrid four-analyzer mass spectrometer of BEEQ geometry (B = magnetic sector, E = electric sector and Q = quadrupole mass analyzer).<sup>41</sup> This instrument was specially designed to study low-energy ion-surface collision phenomena. Primary ions are generated in the electron impact ion source employing 70 eV electrons. The ion beam is accelerated to the desired collision energy and focused at the target surface located in the high- $(1 \times 10^{-8} \text{ Torr})$ chamber vacuum scattering 1 Torr = 133.3 Pa)). Ions scattered from the surface are passed into the second electric sector and finally mass analyzed by a quadrupole mass filter (EQ stage). Both the incident and the scattering angle can be varied independently; however, in the experiments reported here these values were fixed at 55° incident angle (with respect to the surface normal) and 90° scattering angle (with respect to the direction of the incident beam). Data are given in thomson, where 1 thomson (Th) = 1 Dalton per unit charge.<sup>42</sup>

The target employed in this study was a selfassembled monolayer (SAM) consisting of fluorinated alkylthiol supported on a gold film through sulfur linkages,  $CF_3(CF_2)_{11}(CH_2)_2$ —S—Au, prepared by methods described by Chidsey and co-workers<sup>43,44</sup> The surface was rinsed in hexane before being admitted into the scattering chamber. Methane and isotopically labeled methane (<sup>13</sup>CH<sub>4</sub> and CD<sub>4</sub>) were obtained from Cambridge Isotope Laboratories (Andover, MA, USA).

<sup>\*</sup> This definition of chemical sputtering<sup>35</sup> differs somewhat from the definition used by the atomic collision community. For Winters,<sup>36</sup> "if the incoming radiation (ions, electrons or photons) induces a chemical reaction which leads to subsequent desorption of particles, the process could be classified as chemical sputtering". According to Kasi *et al.*<sup>37</sup> "in chemical sputtering, chemical reactions between the incident particles and surface atoms produce molecules which have binding energies to the surface that are low enough for them to desorb at the temperature of the substrate". The above definitions include both the ion/surface reactions (5a and 5b) and chemical sputtering (6a and 6b) as defined above; we distinguish between those two types of processes in that the former yields scattered product(s) consisting of elements of *both* the projectile and the surface, while the latter results in desorbed products involving no part of the projectile.

# **RESULTS AND DISCUSSION**

#### Surface-induced dissociation

Fragmentation of the molecular ion of methane (ionization energy, IE = 12.5 eV) was studied as a function of collision energy; representative data are shown in Table 1 and Fig. 1. Most of the data presented and discussed were obtained using the isotopically labeled form of methane, <sup>13</sup>CH<sub>4</sub>. At the lowest collision energy employed (5 eV), only the scattered projectile ions are observed; at 10 eV, the molecular ion is still present, but extensive fragmentation has already begun. As the collision energy is increased further, no molecular ions survive and lower mass fragments gain in abundance. The appearance energies (AE) of the ions  $CH_3^+$ ,  $CH_2^+$ , CH<sup>+</sup> and C<sup>++</sup>, generated from methane, are known to be 14.4, 15.3, 22.4 and 26.2 eV, respectively.<sup>45</sup> These data, together with comparison with the 70 eV electron impact (EI) data, reveal two major points: (i) the average internal energy imparted to the projectiles by SID at collision energies less than 30 eV is already larger than the energy deposited by 70 eV EI; and (ii) the distribution of internal energies is much narrower in SID than in EI, so much so that there is no SID energy at which all five ions from methane can be simultaneously observed.

For the type of fluorinated surface employed here, previous studies on other ions have found that, on average, 19% of the translational energy is converted into internal energy upon collision,<sup>11</sup> although there have been recent suggestions that this value might be under-estimated.<sup>12</sup> Thus, the range of collision energies from 5 to 40 eV, reported in Table 1, is expected to correspond to the deposition of  $\sim 1-8$  eV of internal energy into the projectile. These values should be considered in light of the activation energy values (AE – IE) for CH<sub>4</sub><sup>+</sup> fragmentation processes (note that the most stable hydrogen products have been assumed):

Process	Activation energy (eV	)
$CH_4^+ \rightarrow CH_3^+ + H$	1 <b>.9</b>	(7)
$CH_4^+ \rightarrow CH_2^+ + H_2$	2.8	(8)
$CH_4^+ \rightarrow CH^+ + H_2 + H_2$	H 9.9	(9)
$CH_4^+ \rightarrow C^+ + 2H_2$	13.7	(10)

Table 1.	SID spectra of CH	∙l₄' ions as a	function of col-
	lision energy*	-	

SID collision energy (eV)				EIÞ		
lon	5	10	20	30	40	(70 eV)
CH‡'	100	70				100
CH₃+		100	100	95	65	85
CH <sup>‡</sup> .		35	55	100	100	9
CH⁺				50	70	4
C+.				10	30	1

<sup>13</sup>CH<sub>4</sub> was used in these experiments. Relative intensities
 (%) are given.
 <sup>b</sup> Data from Ref. 47.

Figure 1. Scattered ion mass spectra obtained upon collision of  $^{13}\text{CH}^+_4$  projectiles at a fluorinated SAM surface at 20, 50 and 80 eV collision energy.

At 5 eV collision energy, the average internal energy deposited is ~1 eV, thus no fragmentation of  $CH_4^+$  is expected, and none is observed (Table 1). At 10 eV, which corresponds to deposition of ~2 eV internal energy,  $CH_3^+$  and  $CH_2^+$  fragments are observed, which is in fair agreement with their thermochemical thresholds of 1.9 and 2.8 eV, respectively (reactions (7) and

(8)), especially if one recognizes that the precursor ion is likely to carry some internal energy prior to the collision. The two lowest mass fragments, CH<sup>+</sup> and C<sup>+</sup>. which require energetic CH4+ ions, do not appear until the collision energy is increased to 30 eV. Using 20%  $T \rightarrow V$  conversion values, this corresponds to an average of 6 eV internal energy deposition with a maximum of perhaps 10 eV, again in reasonable agreement with thermochemical data. Further increases in collision energy cause more extensive fragmentation, as illustrated by the 50 and 80 eV SID spectra of <sup>13</sup>CH<sub>4</sub><sup>+</sup> shown in Fig. 1. In order to be able to distinguish between fragments of projectile ions, and ions originating from the surface or adventitious adsorbate, <sup>13</sup>C methane was used as the sample in these experiments. As noted above, the  ${}^{13}C^{+1}$  peak, due to the complete fragmentation of the projectile, first appears in the scattered ion mass spectrum at 30 eV collision energy; the <sup>12</sup>C<sup>+</sup> peak, which must originate from sputtering of the surface, does not occur until the collision energy is increased to 80 eV. This ability to distinguish between the carbon atoms originating from the projectile and from the surface is very important for elucidating the mechanisms of various processes involved (see below).

A similar series of experiments was performed using methane fragment ions as projectiles. The ions  ${}^{13}CH_3^+$ ,  ${}^{13}CH_2^+$  and  ${}^{13}CH^+$  were each mass selected and collided at the fluorinated SAM surface with translational energies ranging from 5 to 90 eV. Representative scattered ion mass spectra are shown in Figs 2–4. For each of these projectiles, the lowest energy fragmentation process is observed in the 20–25 eV collision energy range, in fair agreement with the relevant thermochemical data, as given below:<sup>46</sup>

$$CH_3^+ \to CH_2^{++} + H \qquad \Delta H = 5.3 \text{ eV}$$
(11)

$$CH_3 \rightarrow CH_1 + H_2 \qquad \Delta H = 5.5 \text{ eV} \qquad (12)$$

$$CH_3^+ \rightarrow C^+ + H_2^- + H^- \Delta H = 9.6 \text{ eV}$$
(13)

$$CH_2 \rightarrow CH^+ + H$$
  $\Delta H = 4.7 \text{ eV}$  (14)

$$CH_2^+ \rightarrow C^+ + H_2 \qquad \Delta H = 4.3 \text{ eV}$$
(15)

$$CH^+ \rightarrow C^{++} + H^*$$
  $\Delta H = 4.1 \text{ eV}$  (16)

While the behavior of these projectiles generally follows trends expected from a knowledge of the underlying thermochemistry, ions are observed in the spectra that point to the operation of complex mechanisms. For example, the ion  $C^{+\cdot}$  from the  $CH_3^+$  projectile is formed in the collision energy range of 30–40 eV, which is lower than expected on the basis of the thermochemistry given in reaction (13). This result may well suggest that a more favorable channel for fragmentation is followed, possibly one that includes an intermediate which involves the surface and the projectile ion (see below).

## Ion-surface reactions

Numerous previous studies have shown that fluorinated SAM surfaces exhibit pronounced reactivity towards a variety of atomic and polyatomic projectiles. In particu-



Figure 2. Scattered ion mass spectra obtained upon collision of <sup>13</sup>CH<sub>3</sub><sup>+</sup> projectiles at a fluorinated SAM surface at 20 eV, 50 eV and 80 eV collision energy.

lar, abstraction of one or more F atoms is commonly observed upon collisions at these surfaces.<sup>31,32</sup>

For the  ${}^{13}C^{+}$  projectile ion, the ion-surface reaction product  ${}^{13}CF^{+}$  (m/z 32) appears in the scattered ion mass spectrum at a collision energy as low as 10 eV.



Figure 3. Scattered ion mass spectra obtained upon collision of  $^{13}CH_2^{+}$  projectiles at a fluorinated SAM surface at 20, 50 and 80 eV collision energy.

This observation is not surprising in view of the favorable thermochemistry for this process. If the thermochemistry of ion-surface reactions are approximated by the known values for similar gas phase ion-molecule reactions, and collisions with  $C_2F_6$  gas are considered in lieu of collisions with the fluorinated surface, the rele-



Figure 4. Scattered ion mass spectra obtained upon collision of <sup>13</sup>CH<sup>+</sup> projectiles at a fluorinated SAM surface at 20, 50 and 80 eV collision energy.

vant thermochemical data for the reactions of all of the methane-derived ions are as presented in Table 2. Note that formation of  ${}^{13}CF^+$  from  ${}^{13}C^+$  projectile is exothermic by a large amount, 52 kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ). As the collision energy is raised to 40 eV, an additional peak appears at m/z 31 and it is attributed to  ${}^{12}CF^+$ , which is most easily interpreted as a product of chemical sputtering of the surface (but see

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Reaction	ΔH° (kcal mol <sup>-1</sup> )*
$C^{++} + C_2F_8 \rightarrow CF^+ + C_2F_8^+$	-52
$CH^+ + C_2F_8 \rightarrow CHF^+ + C_2F_8$	-12
$\rightarrow CF^+ + C_2F_4 + HF$	19
$CH_2^+ + C_2F_6 \rightarrow CH_2F^+ + C_2F_6^+$	-24
$\rightarrow$ CHF <sup>++</sup> + C <sub>2</sub> F <sub>4</sub> + HF	35
$\rightarrow CF^+ + C_2F_8^- + H_2$	48
$CH_3^+ + C_2F_6 \rightarrow CH_3F^{++} + C_2F_6^+$	75
$\rightarrow CH_2F^+ + C_2F_4 + HF$	36
$\rightarrow CHF^{++} + C_2F_5^{+} + H_2$	115
$\rightarrow CF^+ + C_2F_4 + HF + H_2$	108
$CH_4^+ + C_2F_6 \rightarrow CH_3F^{++} + C_2F_4 + HF$	55
$\rightarrow CH_2F^+ + C_2F_5^+ + H_2$	36
$\rightarrow CHF^{+} + C_2F_4 + HF + H_2$	95
$\rightarrow CF^+ + C_2F_5^+ + 2H_2$	108
Data calculated from Ref. 46.	

Table 2. Thermochemical data for reactions of methane generated ions with gaseous  $C_2F_6$ 

below). At 50 eV collision energy, the peaks due to  ${}^{13}CF^+$  and  ${}^{12}CF^+$  have nearly equal abundances (Fig. 5), and this ratio is maintained at all larger collision energies up to 90 eV. The significance of this observation will be discussed later.

In the case of the <sup>13</sup>CH<sup>+</sup> projectile, two ion-surface reaction products are possible (<sup>13</sup>CHF<sup>+</sup> and <sup>13</sup>CF<sup>+</sup>) and both are expected to be observed based on favorable thermochemistry. In fact, only the <sup>13</sup>CF<sup>+</sup> product appears in the spectrum, and it is generated at a collision energy as low as 10 eV. The absence of <sup>13</sup>CHF<sup>+</sup> ions in the scattered ion mass spectra reflects a common feature of ion-surface reactive collisions: intact polyatomic projectiles tend not to pick-up a fluorine atom.<sup>32</sup> In a typical case, the projectile will fragment upon collision, and one or more of the fragments thus formed will undergo reaction with the surface. As indicated in Table 2, the formation of <sup>13</sup>CF<sup>+</sup> is somewhat more energetically favorable than the pick-up of fluorine by the intact projectile. However, this small thermochemical advantage does not determine the behavior of the projectile, as demonstrated by reactions of other methane-derived projectiles. Thermochemically,  ${}^{13}CH_2^+$  is expected to give  ${}^{13}CH_2F^+$  upon collision at the surface, since this process is estimated to be 24 kcal/mol<sup>-1</sup> exothermic; the other two possible ion-surface reaction channels of this ion are both endothermic (Table 2). However,  $^{13}CH_2^+$  does not yield  $^{13}CH_2F^+$  (m/z 34) at any collision energy; indeed, the major product of its ionsurface reaction is <sup>13</sup>CF<sup>+</sup> at all energies, accompanied by a low abundance of <sup>13</sup>CHF<sup>+</sup> product at m/z 33 (Fig. 3).

The <sup>13</sup>CH<sub>4</sub><sup>+</sup> and <sup>13</sup>CH<sub>3</sub><sup>+</sup> projectiles show similar behavior (Figs 1 and 2). Neither of them forms the fluorine adduct ion; but at the lower collision energies examined, formation of the thermochemically most favorable ion-surface reaction product of <sup>13</sup>CH<sub>2</sub>F<sup>+</sup> (m/z 34) is important in both cases. However, as the collision energy is increased (practically for all collision energies above 40 eV), <sup>13</sup>CF<sup>+</sup> becomes the dominant product, although its formation is 108 kcal mol<sup>-1</sup> endothermic. This can be rationalized by the fact that ~20% of translational energy is converted into internal energy; hence there is plenty of energy available for the



Figure 5. Scattered ion mass spectra obtained upon collision of <sup>13</sup>C<sup>++</sup> projectiles at a fluorinated SAM surface at 20, 50 and 80 eV collision energy.

incoming projectile to fragment; once that has happened, it is the  ${}^{13}C^{+}$  fragment which will be most likely to react with the surface, owing to its most favorable thermochemistry (Table 2). However, favorable thermochemistry should be much more important for low-energy projectiles.

The observation that none of the intact projectile ions generated from methane undergoes addition of fluorine emphasizes earlier findings reported in a systematic study of ions containing Group IIIA to VIIA elements.<sup>32</sup> Many polyatomic projectiles, including intact molecular ions of simple compounds, often undergo a formal substitution reaction involving fluorine, rather than simple fluorine addition. For example,  $AlCl_3^+$  projectile yields AlF<sup>+</sup>, AlClF<sup>+</sup> and AlCl<sub>2</sub>F<sup>+</sup>, but not  $AlCl_3F^+$ ;  $PCl_2^+$  reacts with the surface to give  $PClF^+$ and  $PF^+$ , but no  $PCl_2F^+$  is observed, etc. The presence, indeed the predominance, of products obtained by reactions of fragment ions with surface fluorines is of special relevance in seeking the answer to the question of which happens first: projectile fragmentation or ionsurface reaction. It is more difficult to answer this question in cases where both the  $[projectile + F]^+$  and  $[fragment + F]^+$  species are present in the scattered ion mass spectra. Thus, the formation of IF<sup>+</sup> in collisions of CH<sub>3</sub>I<sup>+</sup> at a fluorinated SAM surface could be explained as taking place by either of two routes: (i) fragmentation of CH<sub>3</sub>I<sup>+</sup> to yield I<sup>+</sup>, which subsequently reacts with F from the surface; or (ii) initial formation of  $CH_3IF^+$  (which is observed in the spectrum), followed by subsequent loss of CH<sub>3</sub> to give IF<sup>+</sup>.<sup>29</sup> A number of arguments have been put forward to suggest that sequence (i) is the likely mechanism in a variety of processes,<sup>29,32,48,49</sup> whereas in other cases (ii) is indicated.<sup>29,30,32</sup> In the present case of methane-derived ions, the task seems to be easier, since none of the projectiles exhibits the presence of  $[projectile + F]^+$  products, which may be a strong indication that ion-surface reaction is not the first step in collisions of either projectile.

In addition to this argument, further analysis of the data leads to conclusions supporting a reaction sequence initiated by projectile fragmentation. Thus, in the scattered ion mass spectra of C<sup>+</sup> and CH<sup>+</sup>, ionsurface reaction products (i.e. CF+, CHF+) appear at 10 eV collision energy; the same peaks have a threshold of 25-30 eV when  $CH_2^+$ ,  $CH_3^+$  and  $CH_4^+$  projectiles are employed. One could interpret these observations in the following way: at higher collision energies, the initial products of ion-surface reactions of these projectiles are CH<sub>2</sub>F<sup>+</sup>, CH<sub>3</sub>F<sup>+</sup> and CH<sub>4</sub>F<sup>+</sup>. Since excess internal energy may be present in the products, these species fragment giving rise to CF<sup>+</sup> and CHF<sup>+</sup> products. If this were the case, the gradual decrease in collision energy should bring about conditions whereby  $CH_2F^+$ ,  $CH_3F^{++}$  and  $CH_4F^+$  intermediates are formed with little or no excess internal energy, and these species should be observed in the scattered ion mass spectra. In fact, these species are not observed at any collision energy, so this interpretation does not seem reasonable. The experimental results are best accounted for in terms of the extra energy being required for initial projectile fragmentation. In this way, lower mass fragments such as C<sup>+</sup> and CH<sup>+</sup> are generated, species which exhibit most favorable thermochemistry in reactions with the surface. Indeed, as already pointed out,  $C^{+}$  is the most reactive of the species studied with regards to fluorine abstraction from the surface; consequently, for collision energies above 40 eV, all projectiles derived from <sup>13</sup>CH<sub>4</sub> undergo efficient fragmentation, which subsequently results in <sup>13</sup>CF<sup>+</sup> product formation, which is the dominant feature in all of the spectra above 40 eV (Figs 1-5). Further support for the fragmentation/reaction

sequence comes from the observation that ion-surface reaction products often coincide in threshold energies with the corresponding SID products. For example, in the scattered ion mass spectrum of  ${}^{13}CH_4^+$  ions, the product  ${}^{13}CF^+$  first appears at 30 eV collision energy, which is the threshold energy for the  ${}^{13}C^+$  fragment ion.

While the above arguments support the sequence in which projectile fragmentation precedes ion-surface reaction, a mechanism in which both of those steps take place in a concerted fashion is equally compatible with the experimental observations. However, it is difficult to accommodate the present results with an alternative mechanism in which the projectile fragments after being reflected from the surface inelastically.<sup>50</sup>

A significant observation in all of the spectra shown in Figs 1-5 is the nearly equal abundances of the peaks at m/z 31 (CF<sup>+</sup>) and m/z 32 ( $^{13}$ CF<sup>+</sup>) at higher collision energies ( $\geq 60 \text{ eV}$ ). This result can be rationalized by assuming that at higher collision energies, all projectiles yield  ${}^{13}C^{+}$  as a fragment ion, and that this species can react with the surface to form a symmetrical fluoronium complex such as  $[F^{13}CF^{12}CF]^+$ . A possible mechanism of its formation is proposed in Scheme 1, which illustrates the reaction between a <sup>13</sup>C<sup>+-</sup> projectile ion, labeled as \*C+', and an F-SAM surface, simplified as  $RCF_3$ . In the course of the collision, the highly unsaturated fragment  $C^+$  can form a  $C-F^+-C$  bond at the terminal - CF<sub>3</sub> group through a positively charged fluoronium ion. Subsequent fluorine transfer from an adjacent C-F bond to the labeled carbon, \*C, will result in a new \*C-F bond and leave a free radical site at the terminal carbon. The bond between the carbon and the rest of the alkyl chain, C'R, can break upon the transfer of an electron from R to C, leaving a radical site at R<sup>+</sup> and simultaneously releasing the symmetrical fluoronium complex  $[FC-F^+-*CF]$ . This high-energy complex was not observed, but its fragments were observed. Based on the symmetrical structure, there is an equal posibility that the positive charge will be found in either FC or \*CF group as the complex fragments, generating the observed almost equal abundances of  $CF^+$  and  ${}^{13}CF^+$  peaks in the spectra. Neither  $CF_2^+$  nor  ${}^{13}CF_2^+$  is expected to be formed in significant abundance, since the ionization energy of  $CF_2$  is 11.42 eV,



about 2.3 eV higher than that of CF.<sup>46</sup> Indeed, these species are not observed in the spectra, except for the usual small abundance of m/z 50 (CF<sub>2</sub><sup>+</sup>) due to chemical sputtering of the F-SAM surface. It is also possible that a five-membered ring, which includes a fluorine atom from the second carbon of the SAM chain, is involved in the formation of a fluoronium intermediate. In that case, a 1,2-fluorine migration may occur so that the same complex will result. The proposed scheme does not exclude the formation of other possible fluoronium intermediates, such as  $[^{13}CF^{12}C]^+$  or  $[^{13}CF^{12}CF]^+$ . Both of these species would also be expected to yield equal amounts of  $^{13}CF^+$  and  $^{12}CF^+$ upon fragmentation, and both are actually observed in the scattered ion spectra, albeit at low abundance. Support for the above assignment comes from the observation of an m/z 12 ( ${}^{12}C^+$ ) peak in the 80 eV spectrum of  ${}^{13}C^+$  projectile (Fig. 5). Usually, this peak is the result of hydrocarbon adsorbate sputtering; it accompanies higher mass (and abundance) ions such as  $CH_3^+$ ,  $C_2H_3^+$ ,  $C_2H_5^+$ ,  $C_3H_3^+$ ,  $C_3H_5^+$  and  $C_3H_7^+$ , all of which appear at lower collision energies than C<sup>+</sup>. In the spectrum of  ${}^{13}C^+$  mentioned above, there are virtually no hydrocarbon ions present, pointing to the fact that <sup>12</sup>C<sup>++</sup> in this case is not formed via fragmentation of higher mass hydrocarbon ions, but through a different route, most likely by dissociation of the  $[F^{13}CF^{12}CF]^+$ ,  $[^{13}CF^{12}C]^+$  or  $[^{13}CF^{12}CF]^+$  species invoked above. Given the nature of the processes involved, the  ${}^{12}CF^+$  and  ${}^{12}C^+$  ions are the products of ion-surface reactions, although  ${}^{12}C^+$  in particular does not appear on the face of it to be a reaction product. Other cases in which sputtered products are actually generated by reactions have been reported earlier and the term reactive sputtering which has been used to define this process.<sup>32</sup> It is recognized that it yields products identical with those formed by normal chemical sputtering, but these products have much lower energy thresholds, consistent with the route by which they are formed.32

The mechanism suggested above explains the formation of <sup>12</sup>CF<sup>+</sup> and <sup>13</sup>CF<sup>+</sup> in equal abundances at higher collision energies. However, the <sup>13</sup>CF<sup>+</sup> product ion is observed in the scattered ion mass spectra of <sup>13</sup>C<sup>+</sup> and <sup>13</sup>CH<sup>+</sup> projectiles at collision energies as low as 10 eV, while the <sup>12</sup>CF<sup>+</sup> peak does not appear in the scattered ion mass spectra for these projectiles until a collision energy of 40 eV is reached. These results suggest that <sup>13</sup>CF<sup>+</sup> product ions can be formed through an additional pathway than that involving a <sup>13</sup>C-F-<sup>12</sup>C moiety; for example, the <sup>13</sup>C<sup>+</sup> projectile may bind to the fluorine atom with subsequent <sup>12</sup>C-F bond cleavage, releasing the <sup>13</sup>CF<sup>+</sup> product. Also, the possibility of an electron transfer mechanism, mentioned in the Introduction, can not be excluded for this process.

## **Chemical sputtering**

Peaks due to chemical sputtering represent a common feature in these scattered ion mass spectra. While their overall abundances, and also the relative abundances of various ions, vary as a function of collision energy and the nature of the projectile, the basic pattern of intensities is characteristic of the particular target used. Sputtering is most conveniently studied by employing a projectile that will undergo neither SID nor ion-surface reactions: rare gas ions represent a good choice. Several investigators<sup>40,51,52</sup> have used  $Ar^+$  or  $Xe^+$  for this purpose since several goals can be achieved: (i) the sputtering pattern of a fresh (clean) surface can be measured as a function of collision energy; (ii) surface adsorbate(s) and/or contaminants can be detected, identified and studied; and (iii) surface modification or damage to the surface as the result of prolonged bombardment can be detected and assessed.

Some of these phenomena are illustrated in Fig. 6 for the fluorinated SAM surface. Figure 6(a) was recorded upon collision of 20 eV Xe<sup>++</sup> ions at a fresh surface. The spectrum is dominated by the peak at m/z 69 (CF<sub>3</sub><sup>+</sup>), which is therefore assumed to be the fragment with the lowest energy requirement; weak signals at m/z 31  $(CF^+)$  and m/z 50  $(CF_2^+)$  are just beginning to appear. The only other peak is due to the reflected projectile at m/z 132. As the Xe<sup>++</sup> collision energy is increased, the sputtering peaks increase but they also change in relative abundance; the 60 eV spectrum is shown in Fig. 6(b). New peaks, characteristic of the fluoroalkyl SAM, appear at m/z 81 ( $C_2F_3^+$ ), m/z 93 ( $C_3F_3^+$ ), m/z 100 ( $C_2F_4^+$ ), m/z 112 ( $C_3F_4^+$ ), m/z 119 ( $C_2F_5^+$ ) and m/z 131 ( $C_3F_5^+$ ). Note the absence of an Xe<sup>+</sup> peak at m/z 132, pointing to the fact that practically all incoming projectiles undergo charge exchange with the surface. This is a reasonable observation in view of the thermochemistry involved: the recombination energy of Xe<sup>++</sup> is 12.1 eV, while the ionization energy of the surface fluoroalkane molecules is around 13.4 eV. Thus, at the lowest collision energies, the charge exchange process is endothermic, and therefore, does not occur very efficiently; as the collision energy is increased, energy is channeled into the charge exchange process (In addition, the lack of the Xe<sup>+</sup> signal at higher collision energies may be due to its deeper penetration into the surface). This spectrum shows very little hydrocarbon adsorbate at the surface, a result which is typical of fresh fluoroalkyl SAM surfaces. This same surface was examined again after it had been bombarded for 7 h with a beam of 60 eV  ${}^{13}CH_4^+$  ions, ~10 nA cm<sup>-2</sup> (Fig. (6)c). Two features highlight the changes that have taken place: the abundance of m/z 69 peak has decreased relative to the other sputtering peaks and a new series of peaks have appeared at m/z 27, 29, 41, 43, 55 and 57, indicative of hydrocarbon adsorbate(s). Both of these observations can be rationalized by assuming that the incoming projectiles mainly encounter the terminal CF<sub>3</sub> groups of the self-assembled monolayer, and that one or two fluorine atoms or a CF<sub>3</sub> group are removed by reactions which occur in these collisions. When subject to chemical sputtering by  $Xe^+$ , such a surface will exhibit increased amounts of  $CF^+$  and  $CF_2^+$  ions compared with  $CF_3^+$ . The loss of F atoms upon prolonged bombardment creates active sites at the surface to which adsorbates can bind. The hydrocarbon adsorbate peaks appear at the same mass positions, irrespective of the projectile that is used. This observation suggests that the origin of the adsorbate is intrinsic to the instrumental system: indeed, numerous experiments in different



Figure 6. Scattered ion mass spectra obtained upon collision of Xe<sup>++</sup> projectiles at (a) a fresh fluorinated SAM surface at 20 eV collision energy, (b) a fresh fluorinated SAM surface at 60 eV collision energy and (c) a fluorinated SAM surface following 7 h of bombardment by 60 eV <sup>13</sup>CH<sub>4</sub><sup>++</sup>. (For comparison with (b), the Xe<sup>++</sup> collision energy was also 60 eV.)

laboratories have reached the conclusion that the adsorbate is due to the traces of pump oil vapor present in the vicinity of the target.<sup>52–54</sup> The present experiments also emphasize that the  $C_2$ ,  $C_3$  and  $C_4$  hydrocarbon peaks could not have arisen from the neutralized methane projectile being deposited at the surface.

The pattern of chemical sputtering ion abundances is useful not only in indicating the nature and extent of surface damage,<sup>52-54</sup> but also in verifying surface chemical modification.<sup>40</sup> The data recorded here provide evidence for the modification of the fluorinated SAM surface by methane-derived ions.

### **Deuterated methane**

The main body of experiments was performed with ions generated from <sup>13</sup>CH<sub>4</sub>; in that way, important distinctions between <sup>13</sup>C- and <sup>12</sup>C-containing products could be made. However, in certain cases, ambiguity still existed in that <sup>13</sup>C and <sup>12</sup>CH, <sup>13</sup>CH and <sup>12</sup>CH<sub>2</sub>, etc., are isobars. In order to verify product assignments, a series of experiments were performed using ions generated from perdeuteromethane, CD4, at all collision energies investigated. A comparison of the data obtained from  ${}^{13}CH_4$  and  $CD_4$  is shown in Table 3. The data are not comprehensive; only those peaks are listed for which alternative possibilities introduce ambiguity in interpretation. As can be seen, not all ambiguities are resolved; however, in these cases, the product which includes the projectile carbon atom (the  $^{13}C$ ) is expected to be much more abundant. The ions at m/z 62 and 63 provide a convincing case for projectile carbon atom participation: the  $CD_4^+$  projectile yields a product at m/z 62, which corresponds to  ${}^{12}C_2F_2^+$ .

Table 3. Selected product ions in the mass spectra obtained upon collision of <sup>13</sup>CH<sup>+</sup><sub>4</sub>. and CD<sup>+</sup><sub>4</sub> projectiles at a fluorinated SAM surface<sup>4</sup>

m/z of	Observed prod	uct ions <sup>b</sup>	
product ion	<sup>13</sup> CH <sup>+</sup> projectile	CD <sup>+</sup> projectile	Comments
31	CF	CF	
32	<sup>13</sup> CF, CHF		
33	<sup>13</sup> CHF, CH <sub>2</sub> F	CDF	
34	<sup>13</sup> CH₂F		
35		CD₂F	
45	<sup>13</sup> CCHF, C <sub>2</sub> H <sub>2</sub> F	C,DF	
46	<sup>13</sup> CCH <sub>2</sub> F	-	Not C <sub>2</sub> H <sub>3</sub> F
47	-	C <sub>2</sub> D <sub>2</sub> F	
50	CF <sub>2</sub>	CF <sub>2</sub>	
51	<sup>13</sup> CF <sub>2</sub> , CHF <sub>2</sub>	-	
52	<sup>13</sup> CHF <sub>2</sub>	CDF <sub>2</sub>	Not CH <sub>2</sub> F <sub>2</sub>
62	$(No C_2F_2)$	C <sub>2</sub> F <sub>2</sub>	Includes C atom from projectile
63	<sup>13</sup> CCF <sub>2</sub> , C <sub>2</sub> HF <sub>2</sub>		
64	<sup>13</sup> CCHF <sub>2</sub>	C,DF,	
69	CF <sub>3</sub>	CF <sub>3</sub>	
93 94	C <sub>3</sub> F <sub>3</sub> <sup>13</sup> CC <sub>2</sub> F <sub>2</sub>	C3F3	

a All species listed are singly charged positive ions.

<sup>b</sup> Products due to hydrocarbon adsorbate sputtering have been omitted.

There is no peak at this mass position in the spectrum of the  ${}^{13}CH_4^+$  projectile; but a peak occurs at m/z 63, pointing to the ion composition of  ${}^{13}C{}^{12}CF_2^+$ , i.e. the inclusion of one each of the carbon atoms originating from the projectile and from the surface SAM chain.

Another example of the usefulness of information obtained from labeled ions is provided by the ion  $C_3F_3^+$  (m/z 93). It is present in the scattered ion mass spectra of both  ${}^{13}CH_4^+$  and  $CD_4^+$  projectiles, and is an expected species due to chemical sputtering of the F-SAM surface. However, the spectrum of <sup>13</sup>CH<sub>4</sub><sup>+</sup> projectile shows the presence of an additional peak at m/z 94, corresponding to  ${}^{13}\text{CC}_2\text{F}_3^+$  ion, an ion-surface reaction product containing the projectile carbon. Thus, two types of  $C_3F_3^+$  ions appear in the spectra as a result of two different processes; this fact is concealed in the spectrum due to  $\dot{C}D_4^+$  projectiles since the carbon atoms originating from the surface SAM chain and from the projectile cannot be differentiated. Indeed, these experiments suggest that caution should be exercised in interpreting the scattered ion mass spectra in systems in which the projectile and the surface contain a common constituent. Another interesting observation is the total absence of hydrogen-containing products in experiments done with  $CD_4^+$  projectile. From this, an important conclusion can be drawn: although there is hydrocarbon adsorbate present on the surface, as evidenced by the presence of hydrocarbon sputtering peaks in the scattered ion mass spectra, the adsorbate does not take part in ion-surface reactions observed here, the projectile and the SAM chain are involved exclusively.

# CONCLUSION

Of the various processes that occur upon ion-surface collisions of the title ions, surface-induced dissociation has the lowest energy threshold. In the case of the CH<sub>4</sub><sup>+</sup>, molecular ion, fragmentation is already extensive at 10 eV (nominal) collision energy. The overall SID behavior of this ion, and also of the other ions generated from methane, are fully consistent with earlier findings<sup>11,12</sup> that efficient energy conversion takes place upon collisions at a fluorinated SAM surface. They are in good agreement with the ~20% conversion efficiency value reported earlier and qualitatively support the expectation that a relatively narrow distribution of internal energies is imparted to the projectile ions. None of the intact projectile ions generated from methane

undergoes addition of fluorine without accompanying dissociation. In each case, projectile fragmentation appears to takes place first, and the fragments formed undergo reaction at the surface to pick up a fluorine atom. This sequence of events is borne out further by the fact that formation of a particular fragment ion by SID often coincides (in terms of collision energy) with the appearance of the fluorine adduct of that same ion. These results, however, do not exclude the possibility of projectile fragmentation and ion-surface reaction being concerted.

The processes studied generally have abundances which follow thermochemical requirements. The influence of thermochemistry is particularly evident at low collision energies; at higher energies, translational to internal energy conversion can compensate even for large reaction endothermicities. Formation of the CF<sup>+</sup> product is the most favorable ion-surface reaction. By using <sup>13</sup>C-labeled methane ions as projectiles, it was shown that the mechanism of CF<sup>+</sup> formation involves some kind of a symmetrical fluoronium collision complex, possibly of the type  $[F^{13}C-F^+-^{12}CF]$ . Support for the mechanism proposed is provided by the nearly equal abundances of  ${}^{12}CF^+$  and  ${}^{13}CF^+$  products at higher collision energies, and also by the appearance of  $a^{-12}C^+$  sputtering peak, at an energy lower than needed to observe other sputtering peaks. The use of labeled methane,  $^{13}CH_4$  and  $CD_4$ , pro-

The use of labeled methane,  ${}^{13}CH_4$  and  $CD_4$ , provides some further distinctive advantages in the interpretation of the scattered ion mass spectra. Thus, it was possible to show that the ion at m/z 93 is not a pure sputtering peak, as previously thought, since  ${}^{13}CH_4^+$ . projectile yields peaks at both m/z 93 and 94. The former represents the sputtered  $C_3F_3^+$  ion, but the latter shows the presence of  ${}^{13}CC_2F_3^+$  species, a product of an ion-surface reaction. Experiments with  $CD_4^+$  projectile resulted in an interesting conclusion: all ion-surface reaction products contain deuterium only, and none contains hydrogen, pointing to the fact that no hydrocarbon adsorbate (although present at the surface) takes place in these reactions (i.e. no H-D exchange occurs).

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