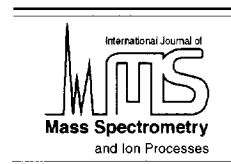




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Chemical transformations of self-assembled monolayers by low energy reactive ion beam bombardment

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Abstract

Reactions of low energy (500 eV) beams of CCl_3^+ , O_2^+ and PCl_3^+ on hydrocarbon and fluorocarbon self-assembled monolayer surfaces are shown to produce chemically modified monolayers. The surfaces before and after the reaction have been characterised by X-ray photoelectron spectroscopy. It is suggested that the surface modification involves the substitution of the ion/surface reaction sites with the appropriate reagent. It appears that the ion beam penetration is minimal and the extent of modification is limited to the top layers of the surface. It is found that the hydrocarbon surface is more reactive than the fluorocarbon surface towards oxygen ions. Upon prolonged bombardment, the alkyl chains desorb and the exposed substrate reacts with the ion beam. It is proposed that extremely thin molecular surfaces of distinct functionality can be made by low energy reactive ion beam bombardment on SAM surfaces.

Keywords: Surface modification; Ion/surface reaction; Self-assembled monolayers; Low energy ion beams; Photoelectron spectroscopy

1. Introduction

Controlled chemical transformation of surfaces has been of interest to science and technology. Methods to achieve this objective vary from the direct exposure of the surface to a chemical reagent to more sophisticated methods such as ion beam implantation [1–3], molecular beam scattering [4,5] and plasma etching [6,7]. Atomic and molecular beams can also be used to effect transformation at appropriate collision energies. The chemistry that occurs at the surface depends on the collision energy, and

consequently by changing this parameter it should be possible to effect specific transformation at the surface. There have been a number of studies in the recent past using ion [8] and molecular [9] beams to effect transformation at surfaces. Almost all of these studies were performed on metals, inorganic compounds and less frequently on polymers. The primary method of characterization involves the analysis of the scattered ion beam. The effect of the transformation on the surface itself was only of secondary concern.

The use of self-assembled monolayers (SAMs) as model surfaces [10] to study chemical processes is currently an active area of research. An important process that occurs when an ion of a few tens of electronvolts collides on such a

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surface is called ion/surface reaction [11]. When appropriate surfaces with various functionalities are used, a number of reactions including hydrogen, halogen and alkyl group abstractions are observed [12]. In addition to atomic ions, polyatomic projectiles have also been used to effect reactions. Most of these reactions appear to proceed through electron transfer in which the surface species gets ionised and the inelastic collision leads to the ejection of a part of the surface which becomes attached to the neutralised projectile in an ion/molecule reaction [11]. After the reaction, it is likely that a radical site is left behind at the surface which may get stabilised by one of the following possibilities: (i) elimination of an atom or group leading to the formation of an unsaturated bond; (ii) reaction with an adsorbate molecule; (iii) reaction with a nearby surface group or molecule [13]. In addition to these possibilities, if a reactive species is available close to the surface site as a result of dissociation of the projectile [14], the radical site can become stabilised by reaction with it [15]. This is a likely process since the reaction and fragmentation occur very close in time or in concert [16]. Ion/surface reaction can also proceed without electron transfer; surface modification occurs via this pathway as well. Recently, one of us has shown that ion/surface reactions can indeed be used to effect transformation of the surfaces [15]. In that study, a fluorocarbon self-assembled monolayer was chemically transformed by reaction with polyatomic projectiles such as SiCl_4^+ , at 60 eV collision energy. While the collision leads to the formation of ion/surface reaction products SiF^+ , SiCF^+ etc., the fragmentation product of the projectile, namely Cl gets attached to the radical site left behind at the surface, causing chemical transformation. However, it is also possible that the ion/surface reaction and the surface modification occur in concert without a prior fragmentation of the projectile.

At collision energies of the order of a few hundred electronvolts, the ion beam is sensitive only to the first few layers of the surface.

Molecular dynamics studies [17] have shown that at 1 keV, 90% of the ejected material in secondary ion mass spectrometry (SIMS) comes from the first layer. At 20 keV, this number is changed only slightly. Therefore the chemical transformations effected on the surface, induced by a low energy reactive ion beam, would be limited to the very top of the surface. By controlling the ion beam, the modification can be laterally resolved. Although the technological importance of spatially resolved transformation is tremendous, there have not been significant efforts in this direction. Among the reasons for the lack of activity are the difficulty in producing intense beams at low energies of a few electronvolts and the relatively poor understanding of the processes which occur upon low energy ion impact on surfaces.

Most of the available reports on low energy ion beam bombardment on surfaces are with atomic beams [8]. The collisions have been performed on metallic or inorganic surfaces in most cases. The use of organic surfaces, also monolayers, in studying reactions induced by molecular ion beams is a very recent area of activity [11–13]. The use of monolayers gives an independent control of the depth of transformation. Moreover, the use of a self-assembled monolayer (SAM) surface having two different chemical species along the alkyl chain, makes it possible to evaluate the effect of ion beam penetration.

In the following, we present a study of the chemical transformations effected on self-assembled monolayers by low energy reactive ion beam bombardment. The surfaces after the reaction were characterised by X-ray photoelectron spectroscopy. Although the low concentrations of the species of interest and the X-ray-induced damage of SAMs at high fluxes impose certain restrictions, the study shows that covalent chemical bonds can be created at the surface by low energy ion beam bombardment. We show that the extent of ion beam penetration is small and the transformations are limited to the very top of the monolayer. It is likely that the

observed surface transformations proceed through ion/surface reactions. The fluorocarbon surface was more resistant to reaction with oxygen ions than the hydrocarbon SAM. The results are in general agreement with the thermochemical data.

2. Experimental

Octadecanethiol used for the preparation of the H-SAM was from Aldrich and was used as such. 1,1,1,2,2,3,3,3,4,4,5,5,6,6,7,7,8,8-Hepta-decafluoro-10-decanethiol was prepared from the corresponding hepta-decafluoro-iododecane using literature procedures [18]. The iododecane was obtained from Aldrich. The purity of hepta-decafluorodecanethiol was ascertained by FTIR and TLC. Gold substrates were prepared by sputtering gold of 1000 Å on to (100) polished Si wafers in an Edwards sputter coater. The Si wafers were pre-cleaned by sonication with trichloroethylene, acetone, concentrated HNO₃, and HF in the order stated. The surfaces were stored in vacuum and were washed with CCl₄ and air dried before immersing in the thiol solutions. One mM solutions of the thiols were prepared in CCl₄ and were used immediately. The surfaces were kept in these solutions overnight, washed in CCl₄ and characterised by X-ray photoelectron spectroscopy (XPS). The SAMs were then removed from the X-ray photoelectron spectrometer chamber, placed in the ion irradiation chamber maintained at high vacuum and reacted with CCl₄, PCl₃ and O₂ ion beams. The ions were produced by a cold discharge of the respective compounds at a pressure of 10⁻³ Torr and were collided with the surface at 500 eV kinetic energy. A beam current of ~0.1 mA was exposed to the surface of 1 cm² area for 1 min to cause the modification. All the products of the discharge were collided with the surface and under the pressure conditions, neutrals may also be involved in the reactions observed. The SAMs were then removed from the apparatus and introduced into

the X-ray photoelectron spectrometer for analysis. Samples were stored in a nitrogen atmosphere if there was any delay between the irradiation and the introduction into the X-ray photoelectron spectrometer chamber.

Monolayers were characterised by X-ray photoelectron spectroscopy using a VG ESCA LAB MKII spectrometer. The spectrometer base pressure was 8 × 10⁻¹⁰ Torr. The photoelectron spectra were measured with Mg Kα radiation at an X-ray flux of 80 W with a pass energy of 20 eV. The X-ray flux was kept low to avoid beam-induced damage to SAMs. The samples were washed in CCl₄ immediately before admitting into the spectrometer. No degassing was observed upon X-ray exposure to monolayers and it was concluded that no significant desorption occurred during the measurement. Also, the intensities of the various peaks remained the same during a day long measurement. All the spectra were average of 10 scans of 60 s duration. The energy scale was calibrated relative to the Au 4f_{7/2} peak at 84 eV. The extent of charging on the monolayer and the gold surfaces varied slightly and as a result the

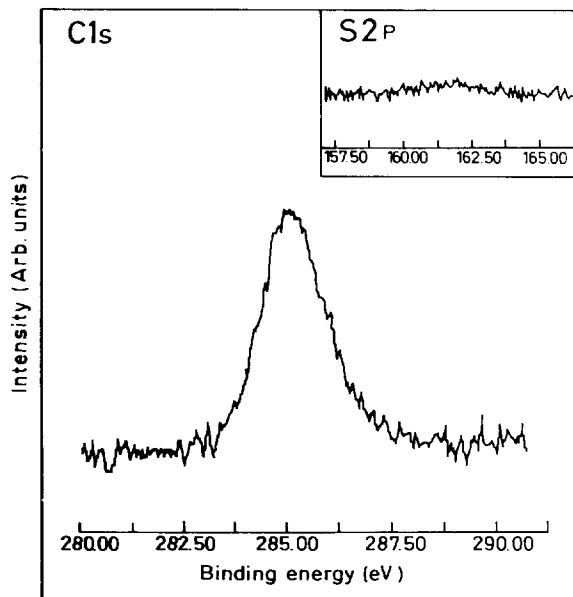


Fig. 1. X-ray photoelectron spectra of the C1s regions of the unreacted octadecanethiolate SAM. S2p is shown in the inset.

binding energies reported have an uncertainty of ~ 0.6 eV. For S2p and Cl2p, the spectra were recorded at a pass energy of 50 eV since the signal quality was poor owing to the low concentration of the species.

3. Results and discussion

In Fig. 1 we show the photoelectron spectra of the C1s and S2p regions of the unreacted octadecane thiolate SAM. The spectra resemble quite closely those reported [19]. The C1s region shows a sharp peak at 285 eV showing that only alkyl carbon atoms are present. The S2p region manifests as a weak feature at 162 eV, which is the same as the expected value for metalthiolate ($RS-M$) or (RS^-M^+) species [20,21]. The low surface coverage of sulphur (in the monolayer structure, not every surface gold atom is covered by sulphur; $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer [22]) and the low X-ray flux (80 W) used to avoid surface damage are the causes for the poor intensity in the sulphur region. The attenuation lengths of photoelectrons of this kinetic energy are in the range of 30–50 Å in Langmuir–Blodgett films [23] and therefore it is not a factor limiting the PE intensity. Although there is a recent report [24] that different sulphur sites are present in the self-assembled monolayer, our spectrometer with an unmonochromatised source is not capable of distinguishing these chemical forms. The SAM shows no oxygen signal as reported before in the case of monolayers grown on gold [19]. No impurities or solvent were detected in X-ray photoelectron spectra. Since the binding energies and peak shapes compare well with those reported [20,21], we believe that the monolayer is ordered. It may be noted that the use of XPS in the characterization of monolayers is well documented [10].

Upon exposure to CCl_4 , the spectra show visible change (Fig. 2). The C1s region is broader compared with the unreacted SAM. It can be seen that the peak maximum appears at 285 eV, and

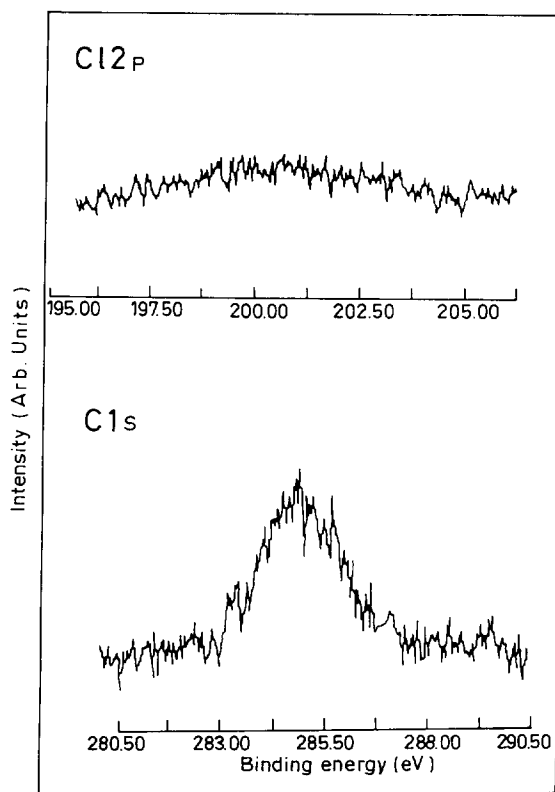


Fig. 2. X-ray photoelectron spectra of C1s and Cl2p regions of the H-SAM reacted with the 500 eV CCl_4 beam. Note that the Cl2p region shows a maximum at 200 eV binding energy.

the structure has a visible high binding energy tail. Clearly, the spectrum has contributions from different types of carbon atoms. The Cl2p region appears as a broad peak centred around 200 eV, corresponding to organic chloride as in polyethylene [25]. The peak suggests that there could be different surface aliphatic chloride species. Another important aspect is that the Cl2p spectrum does not show the presence of any inorganic chloride which would have been observed had the ions interacted with the gold surface. In an independent experiment, it was found that after colliding CCl_4^+ with a clean Au surface, a peak at a binding energy of 198 eV appears due to the inorganic chloride, i.e. $AuCl_3$. The total C1s intensity is marginally reduced compared with the unreacted SAM, suggesting a decrease in surface concentration due to

monolayer desorption. In fact, on further exposure to the ion beam for a period of 5 min, the C1s intensity decreased significantly and subsequent exposure resulted in the formation of AuCl₃ on the surface. In all these reactions, there was no evidence for the presence of unreacted CCl₄ or its fragments on the surface. The pure Au surface also showed no decomposition products of CCl₄ upon ion exposure. Although in the present experiment an analysis of the scattered ions is not possible, it is reasonable to believe that the surface modification other than that due to sputtering occurred through ion/surface reaction involving hydrogen abstraction of the projectile from the surface and the subsequent transfer of halogen atoms to the surface.

Reaction with O₂⁺ has also been performed under identical conditions (Fig. 3). The C1s spectrum of the reacted SAM shows a high binding energy feature at 286.8 eV in addition to the original peak at about 285 eV. This high binding energy peak is close to the reported values [25]

of RCH₂–OH (286.5) and R₂C=O (287.5) functionalities. The O1s region shows a peak at 531 eV, in agreement with the C1s spectrum. As before, the S2p region remains the same showing that the monolayer structure is essentially undisturbed. XPS does not indicate the presence of any other species on the surface. Taken together, XPS suggests that the monolayer functionality has been modified to Au–S–(CH₂)_nOH or Au–S–(CH₂)_{n-1}CHO. There can also be a mixture of both.

In Fig. 4, we show the various XPS regions of the unreacted fluorocarbon SAM. This is the first reported spectrum of the fluorocarbon SAM surface. The C1s peaks are observed at 285 and 291.2 eV, corresponding to the CH₂ and CF₂ functionalities in the unreacted SAM. The integrated intensities of the two peaks are roughly in the ratio 1:4, in agreement with the molecular structure of the SAM, i.e. Au–S–(CH₂)₂–(CF₂)₇CF₃. There was no intensity in the oxygen and iodine regions, indicating that no impurities

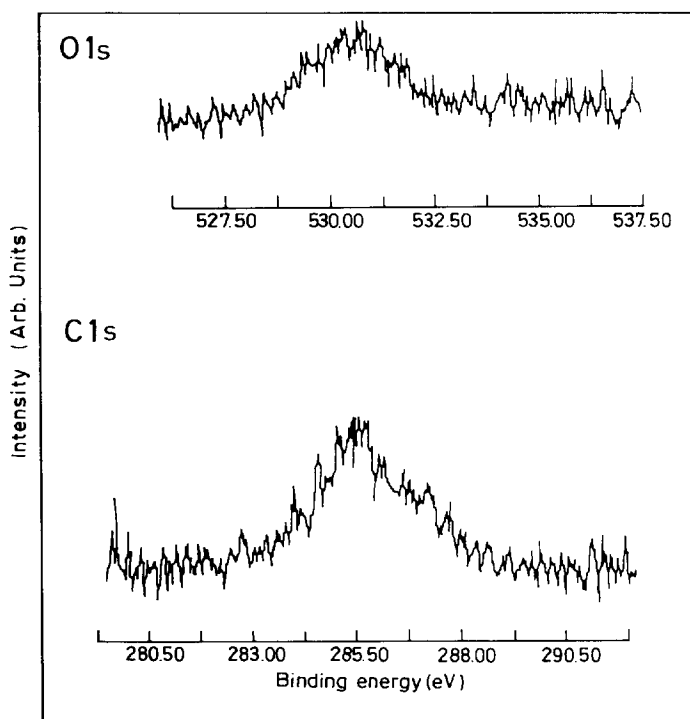


Fig. 3. The C1s and O1s regions of H-SAM after reaction with O₂⁺ beam. Note the shoulder at 286.8 eV in the C1s spectrum.

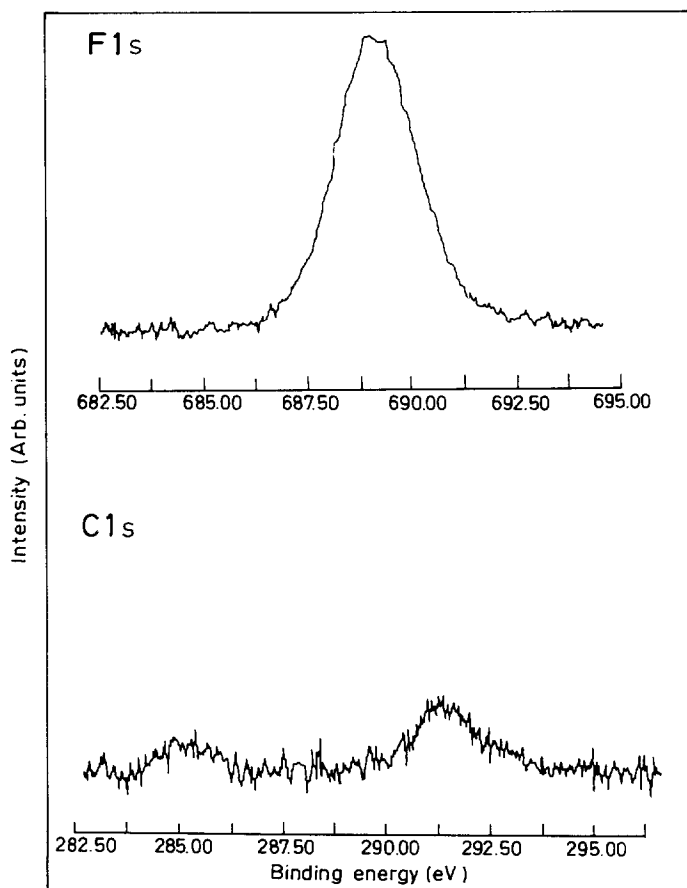


Fig. 4. The X-ray photoelectron spectra of the C1s and F1s regions of the heptadecafluorodecanethiolate SAM.

are present on the surface. The S2p peak appears at 162 eV, at the same value of an alkyl SAM, indicating a similar bonding environment between Au and S. The F1s appears at 689 eV, characteristic of fluorocarbons.

Upon exposure to CCl_4^+ , the spectra show distinct change (Fig. 5). The C1s structure is affected the most. The peak maxima still appear at the same values, but there are considerable differences in the peak shape and relative peak heights. The two peaks are almost similar in intensities, suggesting that it is the CF_2 not the CH_2 carbons that have undergone modification. It may be noted that there is some intensity enhancement at the high binding energy side of the CH_2 peak. The possible species is CCl_2 which has a binding energy of about 287.4 eV [26]. The

other chlorine-for-fluorine substitution product, namely CFC1 , is less likely since it has a binding energy of 290.8 eV [27], where there is no intensity enhancement. The total intensities in the C1s and F1s regions are lower compared to the unreacted SAM, suggesting that some alkyl chains have desorbed upon ion bombardment. The Cl2p structure indeed has some intensity below 200 eV, suggesting the presence of inorganic chloride on the surface. This implies that the ions have reacted with the gold surface exposed as a result of monolayer desorption. The thiolate structure is, however, preserved as evidenced by the S2p feature which still occurs at 162 eV (not shown). It may be noted that the CH_2 functionality is preserved on the surface. This may be taken as evidence for the lack of

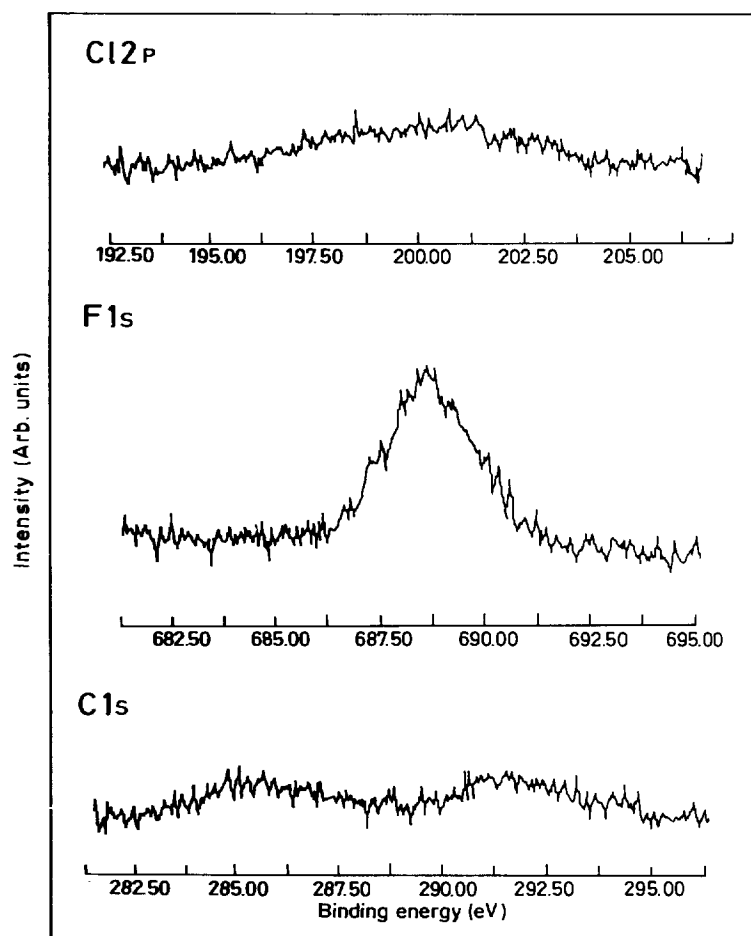


Fig. 5. The X-ray photoelectron spectra of the C1s, F1s and Cl2p regions of the F-SAM after reaction with CCl_4^+ beam. Note that the Cl2p region is broad having multiple contributions.

significant ion beam penetration through the monolayer. Since the CH_2 functionality is preserved, it may be suggested that the upper limit for the ion beam penetration in the F-SAM is of the order of 12 Å, the thickness of the fluorocarbon layer. Electrochemical experiments have also shown that the monolayers are resistant to ion penetration [28].

Upon reaction with O_2^+ beams, no significant change in the surface chemistry is observed (Fig. 6), except that the intensities of the features have decreased. The C1s features are very weak but still appear at the same values as in the unreacted SAM. The F1s structure also appears at the original value. No significant amount of oxygen

is observed at the surface. The results indicate that a substantial fraction of the monolayer has undergone desorption. This is evidenced by the lack of any detectable signal for sulphur. We tried decreasing the exposure time to avoid monolayer desorption; even under this condition, no increase in oxygen signal was observed.

We have also performed reactions with PCI_3^+ beams. The transformations observed were comparable to those observed with CCl_4^+ . XPS investigation did not reveal the presence of phosphorus or its halides on the surface.

The results suggest that the SAMs can be chemically transformed by reactive ion beams. Previous studies of low energy ion beam

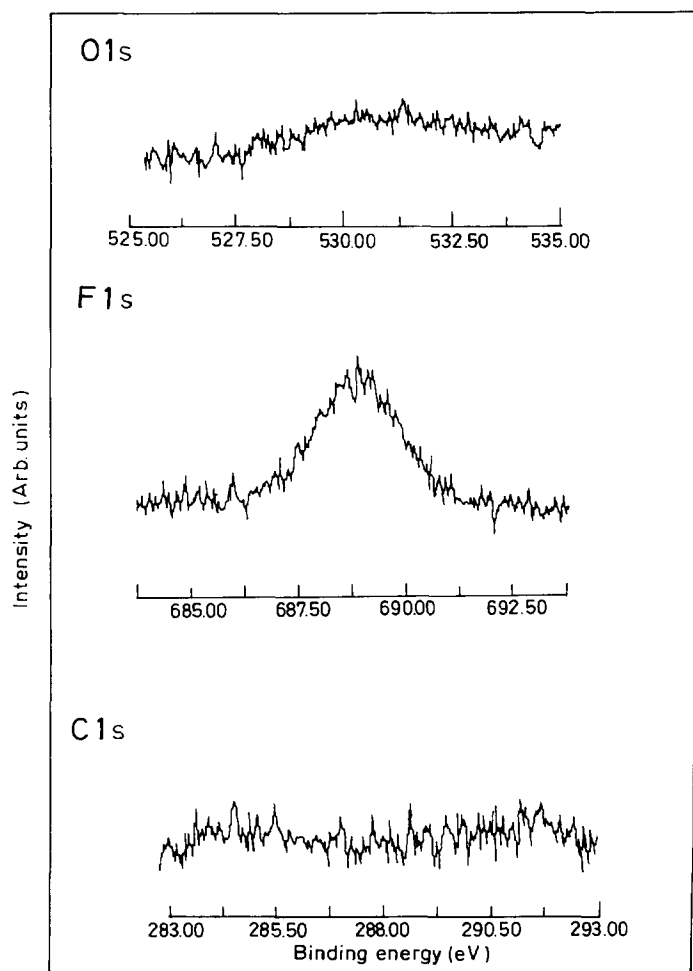


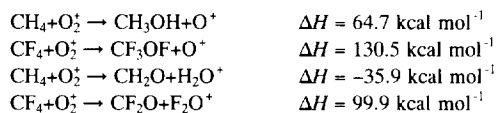
Fig. 6. The X-ray photoelectron spectra of the C1s, F1s and O1s regions of the F-SAM after reaction with O_2^+ beam. Note that the intensity of the C1s and F1s regions are significantly less than the unreacted SAM. Since part of the monolayer has been desorbed due to ion bombardment, concentration of sulphur was low, below the detection limit of the instrument.

bombardment of SAMs have shown that an important event during the ion/surface scattering is reaction. There can be two pathways for reaction, either through electron transfer or through direct oxidative addition. The latter process does not involve electron transfer; the incoming ion gets attached to the surface site and the charge is localised. The ion/surface reaction occurs, resulting in the gas phase ionic species and the neutral modified surface [11]. In both the cases, the surface after reaction is left with a radical site which subsequently undergoes stabilisation. Our results suggest that the surface modifications we

observe are via ion/surface reactions. The primary reason for this conclusion is that the surfaces do not show the presence of any unreacted projectile or its fragment after the ion beam exposure. It may be noted that ion beam scattering experiments also showed no evidence for the accumulation of unreacted projectiles [13,14].

The study shows that the hydrocarbon surface is more reactive towards O_2^+ than the fluorocarbon SAM. The XPS intensities, which are a good measure of the extent of reaction, clearly manifest this. The O1s intensity is especially important since oxygen cannot adsorb on gold and all

the O1s intensity is due to SAM reaction product. It has to be mentioned that the efficiency of charge exchange is higher when O_2^+ collides on H-SAM compared to the collision on F-SAM, due to the lower ionization potential of the former; therefore, while the first process is exothermic or nearly thermoneutral, the latter is endothermic. Note that reaction and charge exchange are two processes, although the former may proceed through the latter (*vide supra*). The ionised surface that is left behind after charge exchange could be excited (most likely vibrationally) which may be one of the reasons for monolayer desorption. Since the F-SAM exhibits more desorption, it may be inferred that the desorption is primarily due to excitation of the surface due to inelastic collision (previous studies show that nearly 70% of the ion collision energy is deposited on the surface [16]) rather than due to a simple charge exchange. However, it is important to point out that both of these desorption pathways need not necessarily require ion penetration. More oxygen intensity for H-SAM may be indicative of reactions and subsequent modifications involving electron transfer. The variation in reactivity can be explained on the basis of thermochemistry also. The ion/surface reactions leading to chemical modification are endothermic in most instances, taking the gas phase thermochemical values [29]. For example, let us consider the gas phase reactions,



Here, the neutral species are assumed to represent the surface. The use of gas phase values are justified because the differences in heat of formation in the condensed phase tend to cancel (since both the reactants and products involve gas phase species). The reaction of O_2^+ with F-SAM is considerably more endothermic than the reaction with H-SAM. The corresponding reactions with neutrals are also endothermic. This correlation

between reactivity and thermochemistry is added evidence for the role of ion/surface reactions in the observed chemical transformations. It may be noted that such correlations are observed in ion/surface reactions.

The reaction of H-SAM with CCl_4^+ leading to the formation of surface-bound chloroalkane involves the formation of a C–Cl bond and the cleavage of a C–H bond, which is energetically not too unfavourable. The corresponding reaction with F-SAM is significantly endothermic due to the differences in the bond energies of the C–Cl and C–F bonds. Thermochemical data suggest that the reactions with the projectile fragments such as CCl_3^+ , Cl^+ and the corresponding neutrals are more endothermic. Thus it is likely that the reactions observed are primarily due to the molecular ions themselves and are driven by the translational energy of the ion.

The fact that the CH_2 functionality is not affected in ion/fluorocarbon surface collisions may be taken to suggest that the ion beam is not sensitive to the deeper atomic layers of the surface. This is also expected from the sputtering yield in SIMS and also from previous studies of surface modification of polymers by reactive ion beams [30]. By controlling the reaction time and the collision energy, it should be possible to effect transformation on the very top atomic layer of the surface.

An immediate extension of the study is to understand the collision energy effects of the transformations. We are also interested in studying the surface by secondary ion mass spectrometry to characterise independently the nature of the transformation. Characterisation of the functional groups by optical spectroscopies and a detailed understanding of the mechanism of the process are also our objectives.

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