ELSEVIER International Journal of Mass Spectrometry and Ion Processes 140 (1994) 177–184

International Journal of Mass Spectrometry and Ion Processes

Short communication

# Surface-induced dissociation and ion–surface reactions at insulating surfaces

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Received 18 January 1994; accepted 21 September 1994

## Abstract

Insulators of macroscopic thickness (e.g. Teflon, adhesive tape) are used for surface-induced dissociation experiments by employing a cloud of low-energy electrons in close proximity to the surface. The spectra that result from collisions of mass-selected ions with these surfaces show molecular ion fragmentation and ion–surface reactions similar to those obtained with related hydrocarbon and fluorocarbon alkanethiolate self-assembled monolayers.

*Keywords:* Surface-induced dissociation; Insulators; Ion–surface collisions; Dimethylsulfoxide; Benzene

Research concerning fragmentation of selected molecular ions by collisions with a surface (i.e. surface-induced dissociation (SID)) has predominantly centered around unmodified metal surfaces [1–7] and self-assembled monolayer films chemisorbed onto gold substrates [7–15]. Other surfaces have been investigated to a lesser extent; these include graphite [16], metal-doped semiconductors and metal oxides [16,17], and thin film coatings of liquid perfluorinated polyethers (Krytox) on stainless steel [18]. The SID technique requires a surface which is capable of maintaining both a voltage load and a zero net charge. The voltage is necessary to integrate the surface into the electric lens setup and therefore acts as an aid in focusing the ion beam, and determining the ion–surface collision energy. A portion of the impinging ion beam loses its charge to the surface in a neutralization process, and it is necessary for the surface to be capable of removing this net charge. Metals were first employed as likely surfaces in SID experiments since they possess both these instrumental requirements. In an attempt to reduce the degree of primary ion beam neutralization and thus improve the SID scattered ion collection efficiency, ordered self-assembled monolayers on gold have been investigated [7–15]. It is believed that the monolayer film acts as an "electron barrier" between the ion beam and the metal surface [12]. However, unlike a true macroscopic insulator, there is still an electrical communication from the monolayer to the metal substrate, a result of electron tunneling [19]

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*SSDI* 0168-1176(94)04081-8

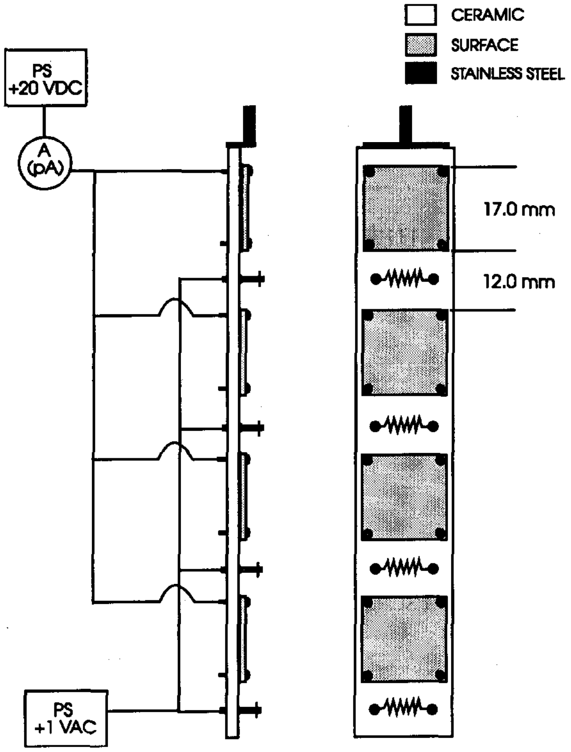

Fig. 1. Surface holder with tungsten filament assembly. Note that individual filaments and surfaces may be electrically isolated with switching assemblies (not shown).

and localized defect sites in the film [20]. The monolayer acts as a "bottleneck", reducing facile electron transfer from the metal to the incoming ion without creating a net charge build-up on the uppermost surface of the film [21].

Until recently, it has been assumed that true insulators would be inappropriate materials to employ as surfaces since by definition they can neither hold a potential load nor conduct current. Here we present a means by which insulators of macroscopic thickness (0.1–1.0 mm), covering a metal support, have been employed as successful surfaces for SID. Spectra are presented here that show molecular ion fragmentation and ion–surface reactions.

When a positive ion collides with a surface, a portion of the incident ions neutralizes. On an insulating surface, it is possible for the charge to remain on the uppermost surface of the insulating layer and distort the electric fields from the underlying metal. The technique employed in this investigation uses a cloud of low energy electrons (about 0–19 eV) from a filament positioned in close proximity to the surface. The electrons act as a counter-charge for the surface charging that occurs. In related work [22–28], insulators have been successfully employed as targets for secondary ion mass spectrometry (SIMS) where the accumulated surface charge has been removed with a focused beam or cloud of electrons. The problem of surface charging experienced in the SIMS experiments, and the application of the electron counter-charge, parallels the situation observed for these SID experiments employing insulator surfaces. However, the goals of the SIMS investigations cited above were to obtain elemental and structural information on the *surface* by chemical sputtering of the surface with high energy (keV–MeV) atomic ions or neutrals. The primary goal of SID experiments is to obtain structural information about the polyatomic projectile ion beam, although surface information is accessible with select reactive projectiles [2,12,13,15].

The original instrumental set-up has been described previously [5]. The surface holder used in these investigations has been modified and is illustrated in Fig. 1. The holder contains four separate surfaces with tungsten filaments positioned equidistant between neighboring surfaces. In this investigation, all four surfaces are electrically linked; however it is possible to isolate them with separate voltage leads. The ion beam has been characterized as a cross-shaped 8 mm × 6 mm beam whose dimensions are smaller than the dimensions of the target surface. The filaments are resistively heated and the resulting electron flux is measured at the surface with a Kiethley 485 picoammeter. To distinguish the current measured from the positive ion beam and the current measured from the electron cloud, the currents associated exclusively with the positive ion beam (measured with the surface filament source off) will be show in the text as positive currents (+nA). The introduction of the counter-charge (surface filament on) reduces the measured positive current. When the electron surface current is greater in magnitude than the positive surface current, the net excess is given in the text as a negative current (−nA to −μA). The filaments are electrically isolated from the four surfaces and may be heated independently of each other, or in various combinations. Only the filaments closest to the surface in the ion optical path are heated. When on, the filaments carry an AC voltage of 0.5–1.5 V.

The systems studied in this investigation include the organic molecular ions of benzene and DMSO-$d_6$. These small ions are employed as probes for organic polymer targets of polytetrafluoroethylene (PTFE) and a hydrocarbon polymer film. SID spectra of benzene and DMSO-$d_6$ have been previously published for surfaces such as unmodified stainless steel [2,5] and *n*-alkanethiolate monolayer films [12,15]. In this investigation, the molecular ion probe is selected with the first quadrupole and allowed to collide with the surface. The laboratory collision energy is dictated by the potential difference between the source and the [metal + insulator] surface. The resulting product ions are analysed by a second quadrupole, positioned at 90° to the first. With the four-surface holder, the instrument may be tuned for a given collision energy using a control surface of known behavior (i.e. a metal or self-assembled monolayer surface), and the insulator surface is then positioned into the ion optical path without changes to the instrument tuning.

For all of the conducting and insulating surfaces investigated in this lab, the 0 eV transmission spectra (i.e. Q1 mass selection of the molecular ion, no surface collision, identical surface and source potentials; figure not shown) contain a single peak, $[M^{\cdot +}]$. Unit resolution is obtained and there are no signs of peak fronting or tailing.

Figs. 2(a)–(d) represent the SID spectra observed for benzene, on a stainless steel surface that has been covered with plastic adhesive tape (Scotch™ Magic Tape; #810 07378-6), without (Fig. 2(a)) and with (Figs. 2(b)–(d)) an applied electron flux. The adhesive tape, approximately 0.1 mm thick, was employed as a crude example of an organic polymeric insulating layer. The adhesive guaranteed intimate contact between the insulator and the metal. To obtain 30 and 70 eV collision energies, the metal surface beneath the tape was kept at a potential of +20 V, and the source potential was floated to +50 V and +90 V, respectively. Fig. 2(a) represents the attempted 30 eV spectrum obtained prior to heating the tungsten filament. The distortion of the *m/z* 78 peak shape and the absence of fragment ion peaks is common to all the collision spectra from insulator surfaces observed in this lab when no surface filament is employed. This effect is observed for benzene and DMSO-$d_6$, as well as for acetone-$d_6$ molecular ion, nitrogen ($N_2^{\cdot +}$) and argon ($Ar^{\cdot +}$) (figures not shown). The peak distortion is only observed for the insulating surfaces, and only when there is a potential difference between the source and surface. The effect is caused by the neutralization of early impinging ions at the surface, and the deflection of later impinging ions by the accumulated charge [21,23]. For the attempted "30 eV collision" in Fig. 2(a), the current measured at the surface was 0.0 nA, i.e. no measurable ion current is hitting the surface. On the octadecanethiolate monolayer surface at 30 eV collision energy with no filament heating, a current of + 18.8 nA was measured. Fig. 2(b) shows the SID spectrum that resulted when the filament was heated and the current measured on the [metal + tape] surface reached −0.5 nA. The current measured here is the sum of the current from the portion of the

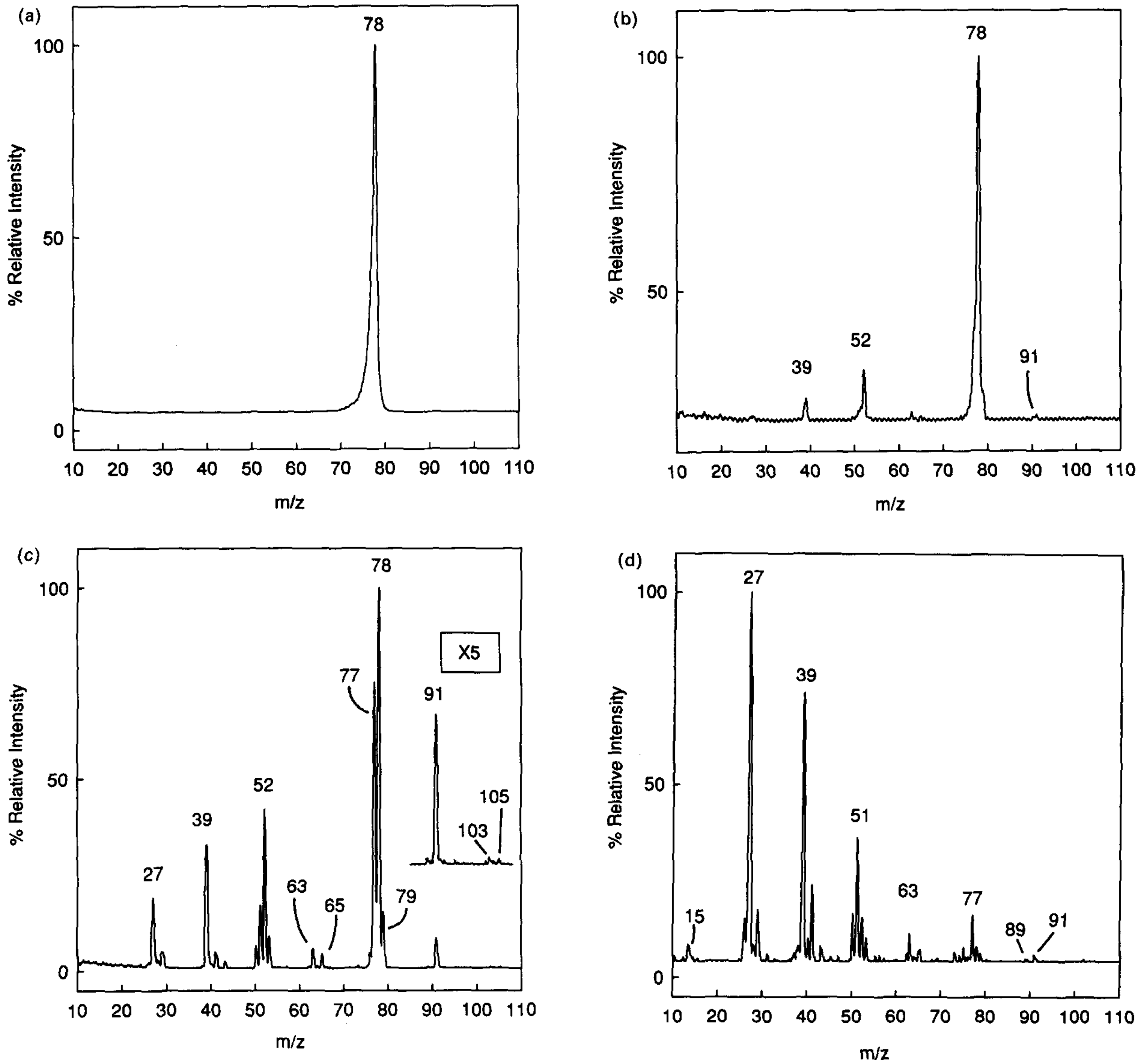

Fig. 2. SID spectrum of benzene (*m/z* 78) on stainless steel covered with adhesive tape. (a) 30 eV potential difference between ion source and surface; surface current = 0.0 nA (filament off). (b) 30 eV potential difference; surface current = −0.5 nA (filament on). (c) 30 eV potential difference; surface current = −6.0 nA (increased resistive heating of surface filament). (d) 70 eV potential difference; surface current = −0.5 nA.

molecular ion beam that has neutralized at the surface plus the electron flux. The spectrum begins to resemble the resolution quality obtained with a conducting surface. A dominant *m/z* 78 peak still exists, however, suggesting that a portion of the ion beam still does not collide with the surface. The effect of increased spectral resolution with increased counter-electron flux has been observed for sputtered ions in SIMS spectra of garnet surfaces [25]. Fig. 2(c) is the spectrum obtained with the surface current reaching −6.8 nA. At this current, the spectrum has unit resolution and clear evidence of both frag-

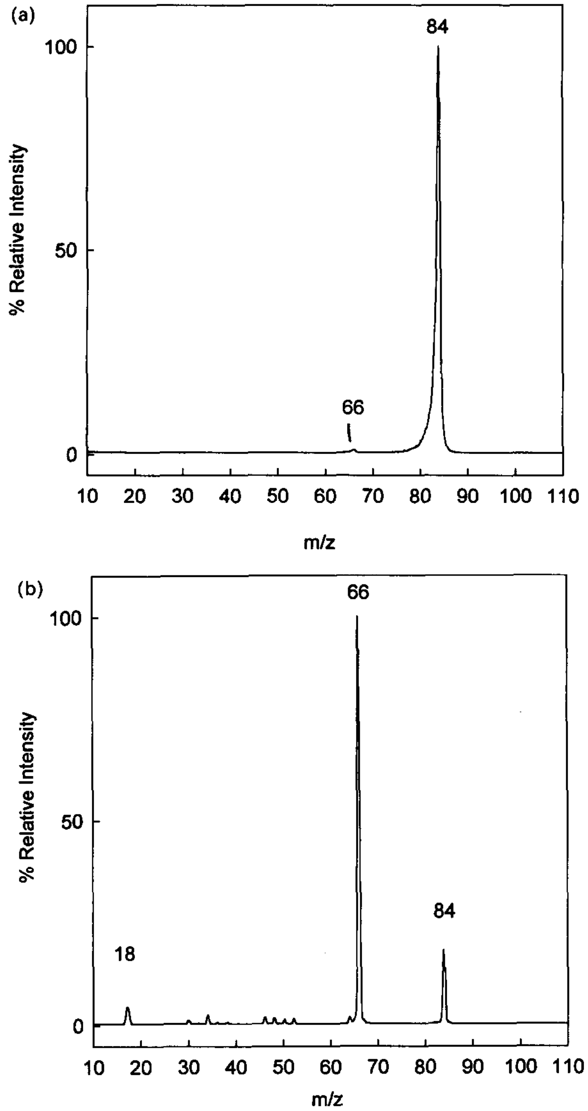

Fig. 3. 20 eV collision of DMSO-$d_6$ (*m/z* 84) on stainless steel covered with 0.1 mm Teflon tape. Measured surface current of (a) 0.0 nA and (b) −0.5 nA.

ment ions common to benzene [29] (e.g. *m/z* 27, 39, 50–53, 63 and 77) as well as ion–surface reaction products [2,7,12] (e.g. *m/z* 65 $[M + CH_3–H_2–C_2H_2]$, 79 $[M + H]$, 91 $[M + CH_3–H_2]$, 103, 105 $[M + C_2H_5–CH_n]$). This spectrum closely resembles 30 eV spectra of benzene with long chain ($(CH_3(CH_2)_nSH)$; $n > 9$) hydrocarbon thiol self-assembled monolayer films [12]. Similar reaction products have been observed for metals covered with hydrocarbon adsorbates, as well as for the alkanethiolate monolayers. As the measured current becomes still greater, the resolution of the spectra remains constant, but the signal intensity decreases. This may be due to an excess of electrons available, causing enhanced neutralization of the incoming ion beam. At current magnitudes greater than −75 nA, the ion signal is no longer measurable at the detector. When the surface filament is switched off, the signal returns to the likeness of Fig. 2(a). Fig. 2(d) is an SID spectrum of benzene on adhesive tape at 70 eV with a surface current of −0.5 nA. Increased collision energies for benzene on tape yield increased relative abundance of low mass fragment ions in the spectra, and this is in agreement with results observed for both unmodified metals and monolayer films [2–5,10–13,15].

Spectra obtained for benzene molecular ion at 30 and 70 eV with a 0.1 mm Teflon surface (Du Pont #T27730A; figures not shown) exhibit fragmentation behavior very similar to that detected with the 2-(perfluorooctyl)–ethanethiolate monolayer, ($CF_3(CF_2)_7(CH_2)_2S$–Au), investigated previously at equivalent collision energies [12]. A greater degree of incident ion fragmentation for a given molecular ion is consistently observed for self-assembled fluorocarbon monolayers, as compared to hydrocarbon monolayers at equivalent collision energies [10–13]. The peak abundances in the 30 eV SID spectra of benzene molecular ion obtained with a Teflon surface are very similar to those observed for the self-assembled fluorinated monolayer, and are indicative of a higher energy deposition than for the adhesive tape surface at equivalent energies. Certain peaks observed in the spectrum acquired on the Teflon surface (*m/z* 31, 45, 57, 70, 95 and 96) do not appear in the SID spectra obtained with adhesive tape, and correlate to the F-containing ions $[CF]^+$, $[C_2H_2F]^+$, $[C_3H_2F]^+$, $[C_4H_3F]^+$, $[C_6H_4F]^+$ and $[C_6H_5F]^+$, respectively [10,12]. These reaction peaks are observed in lower relative abundance with Teflon than for the fluorinated monolayer. The reaction and fragmentation behavior described above suggests a correlation between the Teflon insulator and the fluorinated alkanethiolate monolayer, and the adhesive tape insulator and the hydrocarbon alkanethiolate monolayers.

Fig. 3(a) shows the spectrum obtained for DMSO-$d_6$ at 20 eV on a 0.1 mm thick Teflon surface prior to heating the surface filament. When the current measured at the surface reaches −0.5 nA (Fig. 3(b)), a spectrum containing many fragment ion peaks with unit resolution is achieved. SID spectra of DMSO-$d_6$ from a 2-(perfluorooctyl)- ethanethiolate monolayer have also been reported [15]. The degree of fragmentation observed in Fig. 3(b) is comparable with that observed previously for the fluorinated monolayer at a 20 eV collision energy. Note that no $[M + H]^+$ reaction product ($m/z$ 85) is observed, suggesting little or no hydrocarbon adsorbates present on the surface [15]. A peak at $m/z$ 85 of varying degrees of intensity is observed with DMSO-$d_6$ for adhesive tape, metal, and alkanethiolate monolayer surfaces, and this feature of DMSO-$d_6$ has been used to identify crudely the presence of hydrocarbon on surfaces.

There exists the possibility that the electron cloud present at (or near) the surface may influence the fragmentation spectra observed, either from depositing additional energy to the ions via gas-phase electron–ion collisions (as observed in electron impact ionization sources) or from some neutralization–reionization mechanism. In both cases, the fragmentation spectra could conceivably include an additional energy contribution from the surface electron source. In an attempt to identify whether the ion beam experiences any significant interaction with the electron cloud prior to (or after) collision with the surface, three procedures were attempted.

(i) A 0 eV transmission spectrum, i.e. no surface collision, was taken of DMSO-$d_6$ with both the adhesive tape and Teflon surfaces and the filaments positioned directly above and below the surface were heated incrementally. If the electrons present during the surface collision had influenced the ion beam enough to change the fragmentation spectra, then this contribution would be isolated and present in the 0 eV transmission spectrum. DMSO-$d_6$ was used as a probe of this effect, as it has a low energy fragmentation pathway, $[M-CD_3]^+$; $m/z$ 66 (AE: 0.8 eV) [30]. When the ions experience no surface collision, any fragmentation observed would be associated with an influence from the electron cloud. In addition, the effect should increase with increasing electron flux. The spectra (not shown) yielded only the $m/z$ 84 that was transmitted past the surface, with the same unit resolution quality for 0 nA to −25 mA surface current on both insulator surfaces. No fragmentation ion peak at $m/z$ 66 was observed at any magnitude of surface current investigated. A steady decrease in the detected ion signal was observed however, as the current magnitude was increased from −40 nA to −25 mA. After −25 mA, the ion signal was no longer detectable. The above transmission experiment was also attempted with benzene molecular ion. When the $m/z$ 78 ion was transmitted past the surface (0 eV collision energy) no fragmentation was observed for benzene at any surface electron flux, but the ion signal intensity diminished with surface currents below −40 nA.

(ii) For comparison with the insulator surfaces, a series of 30 eV SID spectra (not shown) were taken for DMSO-$d_6$ and benzene on a 2-(perfluorooctyl)ethanethiolate monolayer surface, also with large filament currents applied to the surface. With currents as great as −2mA, no shift in the relative fragment ion abundances was observed. A steady decrease in absolute signal intensity was observed at negative net currents (30 eV benzene SID on octadecanethiolate monolayer surface with surface filaments off; current = +18.8 Na).

(iii) In an attempt to determine if the electrons in the vicinity of the surface have sufficient energy to ionize neutral sample, the instrument was tuned for a 30 eV collision energy for both DMSO-$d_6$ and benzene, with the Teflon, adhesive tape and fluorinated monolayer surfaces as targets. After the instrument was satisfactorily tuned, the ionization source filaments were turned off, while still leaking in the neutral gas sample. In this way, molecular neutrals were allowed to approach the surface holder with the second quadrupole favorably tuned to collect any existing ion signal. No signal was detected for either DMSO-$d_6$ (IE: 9.0 Ev) [31] or benzene (IE: 9.25 Ev) [31].

According to the evidence presented here (i, ii), the signal loss for both molecular ions in both instances suggests that there is an interaction (neutralization) between the ion beam and the electrons which is independent of the surface. However, the complete absence of any apparent shift in energy deposition in the 30 eV spectrum and the absence of any fragment ions in the transmission spectrum at any surface current suggest that the interaction does not contribute to the fragmentation that is observed. Any influence the electrons may impart to the SID spectra must be less than the energy required to fragment DMSO-$d_6$ to the $CD_3SO^+$ ion (0.8 eV). In (iii), for DMSO-$d_6$ and benzene, the electrons in the vicinity of the surface do not appear to produce an additional ion contribution to SID spectra as a result of ionization of neutral sample species.

It is important to note that the experimental set-up described in the above investigations involved a surface potential of +20 V, and a filament potential of roughly +1 V. The electrons in the vicinity of the surface may therefore have a kinetic energy of 0–19 eV. Should the surface potential be changed to a greater voltage, the above experiments would have to be performed at the new surface potential. It is safe to assume that the greater the surface voltage with respect to the filament voltage, the greater the possibility the electron cloud would affect the SID spectra. At +20 V however, the effect appears to be minimal.

In summary, surface-induced dissociation and ion–surface reactions have been observed for macroscopic, solid insulating surfaces. Adhesive tape and the F-containing polymer Teflon have been shown to act as acceptable SID surfaces when a heated tungsten filament is positioned close enough to supply the surface with a counter-charge to that incurred from the positive ion beam. The quantity and diversity of insulators available as possible surfaces may include other polymers, crystalline salts and ceramics. In addition to tape and Teflon, smooth flint glass (1.0 mm thick) has been investigated in this lab with similar favorable results. The overall scattered ion efficiencies ($E$; the amount of ion signal collected after the surface collision vs. the initial ion signal with no collision) measured for the two insulator surfaces are both 5%. This value is better than those measured for metals (polycrystalline vapor-deposited gold: $E < 1\%$ [32] stainless steel: $E < 1\%$ [2]) however they are less than those regularly observed for monolayer surfaces [12] (octadecanethiolate; $CH_3(CH_2)_{17}S$–Au: 13%, 2-(perfluorooctyl)-ethanethiolate; $(CF_3(CF_2)_7(CH_2)_2S$–Au: 63%). It is important to mention that the instrumental set-up employed here for insulator surfaces is far from ideal. The scattered ion efficiency for both the Teflon and hydrocarbon polymer surfaces is the same value. This implies that neutralization of the molecular ion beam at the surface is presently dictated by the electron flux, and not the work function of the polymer surfaces. This is in contrast to results for self-assembled monolayers. With an improved electron source (one able to control and focus the electron flux better), neutralization as a result of excess electrons will be diminished. It is believed that this will increase the measured scattered ion efficiency to values dictated by properties inherent to the insulator (e.g. surface work function, etc.).

## Acknowledgments

We would like to acknowledge and thank Dr. John B. Fenn for several fascinating discussions concerning ion–surface interactions, and for offering the original idea of using an insulator–filament assembly as a likely SID surface. This work was supported by the National Science Foundation (grant number CHE-9224719).

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