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Collisions of $C_{60}^{+\bullet}$ and C_{60}^{2+} at Fluorinated and Non-fluorinated Self-assembled Monolayer Films[†]

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We report here the spectra that result when singly and doubly charged buckminsterfullerene ions, $C_{60}^{+\bullet}$ and C_{60}^{2+}, collide with self-assembled monolayer films at collison energies ranging from 125 to 320 eV. The surfaces were prepared by the spontaneous assembly of octadecanethiol ($CH_3(CH_2)_{17}SH$), perdeuteroeicosanethiol ($CD_3(CD_2)_{19}SH$), and 2-(perfluorooctyl)-ethanethiol ($CF_3(CF_2)_7CH_2CH_2SH$) on vapor-deposited gold. The fluorinated surface causes the greatest conversion of kinetic energy into internal energy; more extensive fragmentation of doubly charged buckminsterfullerene C_{60}^{2+} is detected in collisions with this surface than in collisions with the alkanethiolate surfaces.

Recent work by several groups has shown that low-energy collisions between polyatomic ions and surfaces can produce fragmentation useful for structural characterization of ions.[1–20] This technique, introduced and developed by Cooks and coworkers, is known as surface-induced dissociation (SID) and has been reviewed recently.[1] It has been shown that SID can produce relatively extensive fragmentation of species including benzene,[1,5,14,16,19a,20] polycyclic aromatic hydrocarbons,[1–3,14,19a] and peptides;[2,11b,12,18c] in the case of peptides, low-energy collisions with surfaces have been used to extract sequence information. Ion/surface collisions result in other phenomena as well, including chemical sputtering, charge exchange, and ion/surface reactions.[1] These phenomena can have an important influence on the products of ion/surface collisions; for, example, molecular ions of pyridine extract a hydrogen from some surfaces and fragment from an excited protonated species.[1,13] Moreover, processes such as charge exchange between the projectile and the surface can influence the product yields (through neutralization).

SID is proving to be a useful tool in structural characterization problems because a significant fraction of the kinetic energy of impact is deposited into the projectile as internal energy. The fraction of kinetic energy converted to internal energy is relatively high, typically 12–15% for small molecules.[1] Thus, if the efficiency of energy transfer holds for larger species, SID may be a useful method for depositing relatively large amounts of energy into large or non-labile species with instruments that utilize low ion energies. A particularly intriguing feature of SID is that the efficiency of energy transfer appears to increase with projectile mass, based on a limited number of studies to date. Whetten and coworkers, for example, have estimated that as much as 35% of the kinetic energy is converted to internal energy when large alkali halide cluster ions (e.g. masses areater than 200 u) strike surfaces.[21] The high relative energy transfer in ion/surface collisions makes them attractive for the study of ions that are relatively difficult to fragment in conventional spectrometers on the time scale of the mass spectrometric experiment. This is the case for large molecules, where activation energies for fragmentation may be relatively low, but the number of degrees of freedom are large (hence the rate of dissociation is low). Alternatively, SID may be useful in probing ions that have relatively high activation energies for fragmentation. The latter is the case for buckminsterfullerene, C_{60}.

In early photodissociation studies on $C_{60}^{+\bullet}$ formed by laser vaporization, Smalley and coworkers showed that fragmentation of $C_{60}^{+\bullet}$ occurred by multiple C_2 loss to yield ions as small as $C_{32}^{+\bullet}$, and further fragmentation beyond this point yielded even- and odd-number carbon cluster ions.[22] They estimated that 18 eV was an upper limit for the activation energy for C_2 loss. The discovery of a synthetic technique for the bulk synthesis of buckminsterfullerene[23] has led to many subsequent studies of the fragmentation behavior of the fullerenes and both high- and low-energy collisions have been used to probe C_{60} fragmentation (see Refs 24a and 24b for reviews of the area). Initial gas-phase collision studies utilized kilovolt collisions with target gases such as helium and oxygen.[25,26] Successive loss of C_2 was observed,[25] and in the case of collisions with oxygen, kilovolt collisions were sufficient to fragment $C_{60}^{+\bullet}$ to yield small fragments with even and odd numbers of carbons.[26] Heavier target gases, such as xenon, have been used to fragment $C_{60}^{+\bullet}$ at lower collision energies,[27,28] and loss of C_2 has been observed at collision energies near 150 eV using xenon under multiple-collision conditions.[28] In general, collision-induced dissociation (CID) studies largely confirmed the early photodissociation work by Smalley's group. However, the remarkable stability of C_{60} towards fragmentation by collisions was again shown by the fact that keV collisions of C_{60} with helium can result in the uptake of the helium atom, resulting in the formation $C_{60}He^+$.[29,30] In some cases, as much as 44 eV (the center-of-mass collision energy at 8 keV in collisions of C_{60} with He) is taken up when such gas-phase endohedral complexes

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are formed, yet the resultant ion survives on the microsecond time scale. Recently, this technique has been used to probe fullerene structures that do not obey the isolated pentagon rule (e.g. C_{58}, C_{68}), and these structures do not take up He and survive intact.[31] This further demonstrates the well-known and special stability of fullerene cages which obey the isolated pentagon rule.

Several investigators have also studied collisions of fullerene ions with surfaces of various types.[15,32–39] Mowrey and coworkers have also used molecular dynamics to model C_{60} collisions with surfaces.[40] They were able to estimate that approximately 18–28% of the translational energy is converted to internal energy in such collisions, although their computational timeframe was too short to observe fragmentation. Subsequently, Whetten and coworkers showed that $C_{60}^{+\bullet}$ is very stable towards fragmentation in surface collisions with silicon and graphite surfaces, and in their initial study, they reported that fragmentation was not observed at collision energies below 200 eV (using graphite and silicon surfaces).[15] Even at higher collision energies, no substantial fragmentation was observed. Observations of electron emission from $C_{60}^{-\bullet}$ after collisions with surfaces suggested that energy deposition of the order of 25–30% of the collision energy was not unreasonable. Similar results have been reported by Hertel and coworkers in collisions of $C_{60}^{+\bullet}$ with highly oriented pyrolytic graphite (HOPG) surfaces.[36,37] These studies also showed that collision energies below 200 eV produced no fragmentation, although collision energies of 275 eV or greater resulted in fragmentation of $C_{60}^{+\bullet}$. Using fragmentation data obtained at 455 eV and an estimated energy conversion of 18% (based on the simulations of C_{60} collisions with surfaces by Mowrey and coworkers),[40] these workers used simplified RRKM theory to estimate the dissociation barrier for the loss of C_2 to be 10 eV, consistent with the relatively high activation energy for C_2 loss estimated by Smalley and coworkers.[22] More recent work by the Whetten group has further considered electron emission from negatively charged fullerenes, which they have used to place an upper limit of 50% on the conversion of translational energy to internal energy.[32,33] These estimates of internal energy deposition, while consistent with other SID data, lead to estimates of activation energies for C_2 loss that are higher than those measured by other techniques. For example, Lifshitz and coworkers have recently used kinetic-energy-release data to estimate the activation energy for C_2 loss at less than 6 eV.[41] Experimental and theoretical investigations are continuing in this area in attempts to reconcile these disparate activation energy estimates.

Recent work by the Cooks group, and by Wysocki and coworkers, indicates that the projectile ion is not the only factor that influences the energy transfer in ion/surface collisions.[17–20] Self-assembled monolayer films, prepared by the spontaneous covalent assembly of 1-alkanethiols to gold or silver,[42–52] have been successfully utilized as collision surfaces.[16–20] Recent studies with fluorinated self-assembled monolayers (e.g. $CF_3(CF_2)_nCH_2CH_2SAu$) indicate that the energy transfer is significantly higher when a projectile strikes fluorinated monolayer surfaces compared with collisions at the same energy with stainless steel or alkanethiolate surfaces.[17,19,20] Cooks and coworkers have estimated that the energy transfer increases from approximately 12% to 17–20% when $W(CO)_6$ (a reasonably well-characterized thermometer molecule) strikes a fluorinated surface.[19a] These workers have also observed results with pyrene that suggested, for some molecules, as much as 50% of the kinetic energy was converted to internal energy. The origin of the increased energy transfer may arise from at least three sources: (i) the increased mass of the target atoms that the projectile atoms are striking; (ii) the increased rigidity of the fluorinated monolayer surface; and (iii) the higher ionization energy of the fluorinated monolayer surface.[19,20,53,54]

Buckminsterfullerene (C_{60}) provides a challenging system for which the relative extents of fragmentation and neutralization can be compared on the two different types of monolayers, i.e., alkanethiolates and fluorinated alkanethiolates. We report here the result when singly and doubly charged buckminsterfullerene, $C_{60}^{+\bullet}$ and C_{60}^{2+}, collide with self-assembled monolayer films at collision energies in the range of 125–320 eV. The monolayer films used in this study were prepared from octadecanethiol ($CH_3(CH_2)_{17}SH$), perdeuteroeicosanethiol ($CD_3(CD_2)_{19}SH$), and 2-(perfluorooctyl)-ethanethiol ($CF_3(CF_2)_7CH_2CH_2SH$) on vapor-deposited gold. The results on the two types of surfaces are compared with SID data from the Literature to provide further insight into the unique stability of buckminsterfullerene and illustrate the dramatic influence that the nature of the surface can have on SID spectra.

RESULTS

The SID spectra of doubly charged buckminsterfullerene, C_{60}^{2+}, obtained at 250 eV collision energy by using octadecanethiolate and 2-(perfluorooctyl)-ethanethiolate surfaces are shown in Fig. 1(a) and (b) respectively. The behavior C_{60}^{2+} in collisions with the octadecanethiolate surface (Fig. 1(a)) is similar to that previously observed with stainless steel under conditions in which the stainless steel is expected to be coated with physisorbed hydrocarbon contaminants.[34] The primary feature of the spectrum obtained on the octadecanethiolate surface is charge reduction; $C_{60}^{+\bullet}$ is the major product detected. The relative stability of the $C_{60}^{+\bullet}$ ion is apparent from this spectrum; even at a collision energy of 250 eV, only a low abundance of a fragment ion, $C_{58}^{+\bullet}$, resulting from C_2 loss, is observed. Peaks corresponding to ions of low mass appeared with surface collisions of both $C_{60}^{+\bullet}$ and C_{60}^{2+}; these are attributed to (chemical) sputtering of physi- or chemisorbed surface materials and accounted for roughly 25% of the total ion abundance.

Figure 1(b) shows the SID spectrum for a 250 eV collision of C_{60}^{2+} with the fluorinated surface. The spectrum is characterized by significantly more fragmentation than was observed at similar collision energies on the stainless steel and octadecanethiolate surfaces. For example, singly charged fragment ions are observed that correspond to the loss of greater than ten C_2 units ($C_{46}^{+\bullet}$). Moreover, doubly charged fragment ions are also observed in the spectrum and the extent of fragmentation varies with collision energy as illustrated in Figs 1(b) and 2. The results (numbers not shown) also indicate that total scattered-ion abundance is higher for

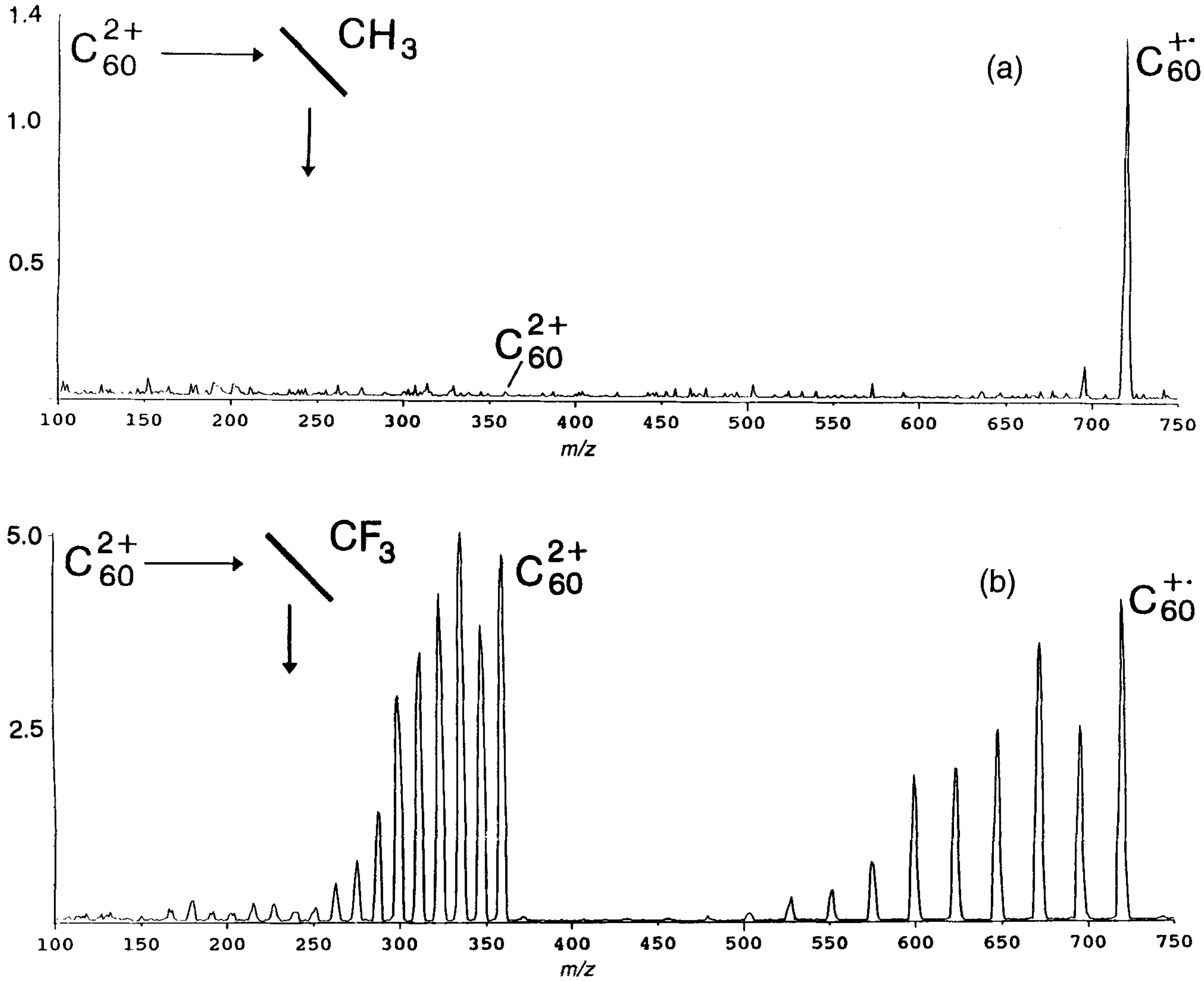

Figure 1. Ion/surface collision spectra obtained by colliding C_{60}^{2+} at 250 eV collision energy with a surface prepared from (a) octadecanethiol and (b) 2-(perfluorooctyl)-ethanethiol on vapor-deposited gold.

the fluorinated surfaces (i.e., neutralization is decreased), a result that is consistent with previous observations on other systems.[19,20]

An interesting feature of the spectra obtained at higher collision energies, and particularly the spectrum obtained at 320 eV (Fig. 2(b)) is the relative abundance of ions in the low-mass region below *m/z* 360. Because only carbon atoms are involved, ions in this region may correspond to overlapping singly and doubly charged ions (e.g., $C_{11}^{+\cdot}$ and C_{22}^{2+} will have the same value of *m/z*). However, anomalously high abundances at *m/z* 132, 180 and 228 suggest that these are probably $C_{11}^{+\cdot}$, $C_{15}^{+\cdot}$ and $C_{19}^{+\cdot}$, as these are well known carbon-cluster magic numbers. Similar results have also been observed in the fragmentation of C_{60}^{2+} in gas-phase collisions with oxygen, where charge reduction and fragmentation to yield small singly charged clusters has been observed.[26] By contrast, ions at *m/z* 348, 336 and 324 are most likely to be due to doubly charged ions, since significant abundances of species such as $C_{29}^{+\cdot}$ and $C_{27}^{+\cdot}$ have not been observed in dissociation spectra obtained by a number of different methods.

Figure 3(a) and (b) show the results of collisions of singly charged C_{60} with the *fluorinated* surface. The results show that low abundances of fragments can be observed at collision energies as low as 125 eV. This is an approximate measure of the threshold for the appearance of fragments (we see little fragmentation below ≈100 eV collision energy). This approximate threshold is considerably lower than has been observed for $C_{60}^{+\cdot}$ on other types of surfaces.[15,40] Note also the relative absence of fragmentation of C_{60}^{2+} at 250 eV for the *octadecanethiolate* surface in Fig. 1(a). Figure 3(a) and (b) also show the effect of increasing the collision energy on fragmentation of the singly charged ion; in particular, the ratio of C_{56}^{+} to C_{58}^{+} changes significantly with collision energy.

Peaks higher in mass than the selected projectile ion (e.g., *m/z* 744) are detected in some of the ion/surface collision spectra (Figs 1(b) and 2(b)). These presumably correspond to ion/surface *reaction* products and appear at an interval of 2 carbons from$C_{60}^{+\cdot}$ and C_{60}^{2+}; a possible source of the C_2 units that are added is the deposition of C_{60} and its fragments on the surface. Of particular note is the ion observed at *m/z* 372 in Fig. 2(b). If this is a singly charged fragment, it corresponds to $C_{31}^{+\cdot}$, an odd-numbered fragment that is not observed in significant abundance in gas-phase collision spectra of $C_{60}^{+\cdot}$. This would suggest that it is more likely from C_{62}^{2+}, corresponding to a C_2 pickup product and consistent with the observation of the ion at *m/z* 744. Hertel and coworkers have observed expansion of $C_{60}^{+\cdot}$ to $C_{120}^{+\cdot}$

in collisions of $C_{60}^{+\bullet}$ with fullerene-covered surfaces,[39] and a similar phenomenon may be occurring here with smaller building blocks. Systematic investigation of these reactions is planned for the future.

DISCUSSION

The effect of the surface composition on fullerene fragmentation behavior is manifested in two ways. The most direct effect of using the fluorinated surface is the appearance of the doubly charged ion and its fragments in the SID spectrum of C_{60}^{2+}. This may be attributed to the higher ionization energy for the fluorinated surface, as compared with that for either the octadecanethiolate surface or hydrocarbon-contaminated stainless steel. The first ionization energy for C_{60} is known to be 7.6 eV.[55] There is some question as to the ionization energy of $C_{60}^{+\bullet}$ ($C_{60}^{+\bullet} \rightarrow C_{60}^{2+}$), which has been variously measured to be 9.7 eV,[34a] 11.9 eV[56] and 12.25 eV,[57] depending on the technique employed. However, all the estimates of the second ionization energy of C_{60} are comparable to, or higher than, the estimated ionization energies (IE) for either the octadecanethiolate or stainless steel surfaces (e.g., IE[$C_{10}H_{22}$] = 9.65 eV). Thus, significant reduction of the doubly charged ion at the surface is expected, consistent with the observation that only singly charged ions are observed as the products of collisions of C_{60}^{2+} with these surfaces. By contrast, the higher ionization energy for the fluorinated surface (e.g., IE[C_3F_8] = 13.4 eV) reduces the likelihood that charge reduction will occur when C_{60}^{2+} approaches the surface, with the resultant observation of reflected C_{60}^{2+} and its doubly charged fragments. Of course, similar arguments can be made for the singly charged ions $C_{60}^{+\bullet}$. There is less neutralization of $C_{60}^{+\bullet}$ in collisions with the fluorinated surface, as compared with stainless steel or alkanethiolate surfaces, which would improve the signal-to-noise ratio for the observation of products. Improvements in signal-to-noise ratio could partially account for the observation of fragments at lower threshold collision energies with the fluorinated surface; however such arguments do not explain the significant changes in the ratios of fragment-ion abundances from fluorinated surfaces, as discussed below.

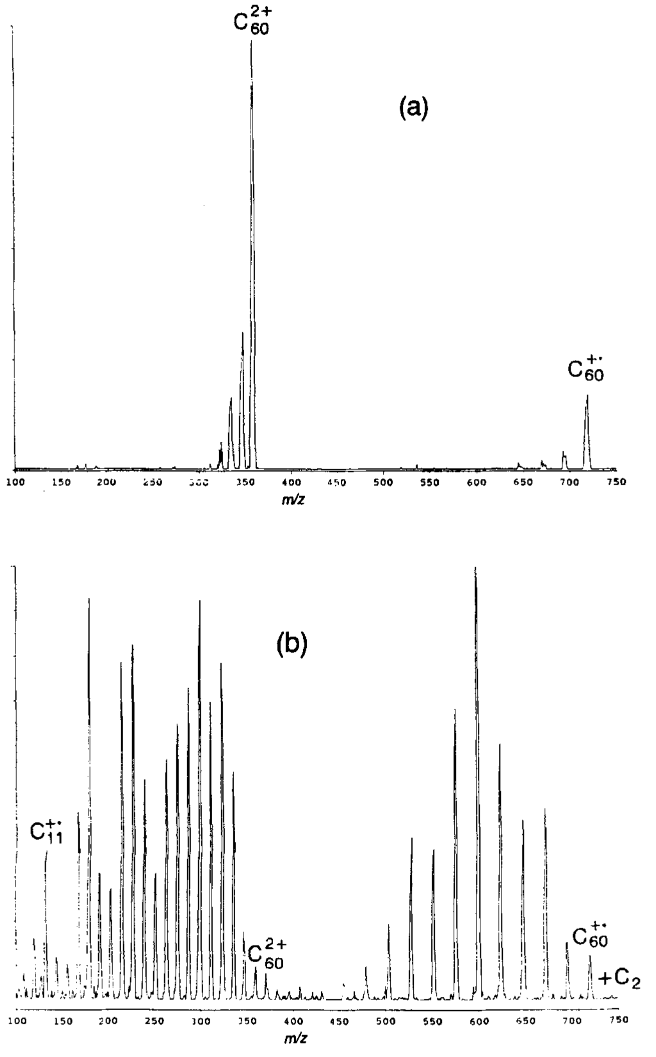

Figure 2. Ion/surface collision spectra obtained by colliding C_{60}^{2+} at (a) 180 eV and (b) 320 eV collision energies with a surface prepared from 2-(perfluorooctyl)-ethanethiol on vapor-deposited gold.

As was the case with benzene[19,20] and other molecules, the fluorinated alkanethiolate surface also appears to result in an increase in the translational-to-internal energy transfer in surface collisions of C_{60}. Fragmentation is more extensive and relative product abundance ratios are altered enough that the results are consistent with greater energy deposition at any given energy. For example, the ratio $C_{58}^{+\bullet}:C_{56}^{+\bullet}$ resulting from fragmentation of C_{60} appears to be an indicator of internal energy deposition. Similar shifts have been observed with increases in the translational energy of gas-phase collisions between $C_{60}^{+\bullet}$ and Xe (e.g., the $C_{58}^{+\bullet}:C_{56}^{+\bullet}$ ratio shifts from 3:1 to nearly 1:1 as the collision energy is increased from 100 eV to 190 eV under multiple-collision conditions in a triple quadrupole instrument).[28] The $C_{58}^{+\bullet}:C_{56}^{+\bullet}$ ratio resulting from collisions of $C_{60}^{+\bullet}$ with the fluorinated surface (Fig. 3) exhibits similar behavior, shifting from 5:1 at 125 eV to 1.6:1 at 160 eV. Thus, a direct comparison of the results in Fig. 1 suggests significantly higher energy deposition from the fluorinated surface; the ratio of $C_{58}:C_{56}$ fragments (either singly or doubly charged) is less than 1, while the ratio of $C_{58}:C_{56}$ fragment ions from the octadecanethiol surface must be considerably greater than 1 (based on the absence of a measurable abundance of C_{56}). This higher energy transfer is consistent with the results of previous studies of these surfaces.

This raises a larger question: what is the actual energy transfer for an ion such as $C_{60}^{+\bullet}$? As noted above, previous estimates of the energy transfer for surface collisions have been in the range of 12–50% and a barrier height of roughly 10 eV has been estimated[37] for the loss of C_2 from $C_{60}^{+\bullet}$ (based on experimental data and unimolecular reaction rate theory).[58] This barrier is thought to be consistent with the bond-breaking necessary to initiate loss of C_2. The results reported here show that with the fluorinated surface, fragmentation of $C_{60}^{+\bullet}$ can be observed with collisions of roughly 125 eV. This is considerably lower than the energies at which fragmentation has been observed in other surface studies.[15,36,37] Part of this effect can be explained by higher initial internal energies for the C_{60} ions in this study, since they are formed by thermal desorption/electron ionization. By contrast, the ions in Whetten's experiments were formed by laser desorption and entrainment in a molecular beam,[15] so they are internally cooler. Thus, it is expected that ions in this study

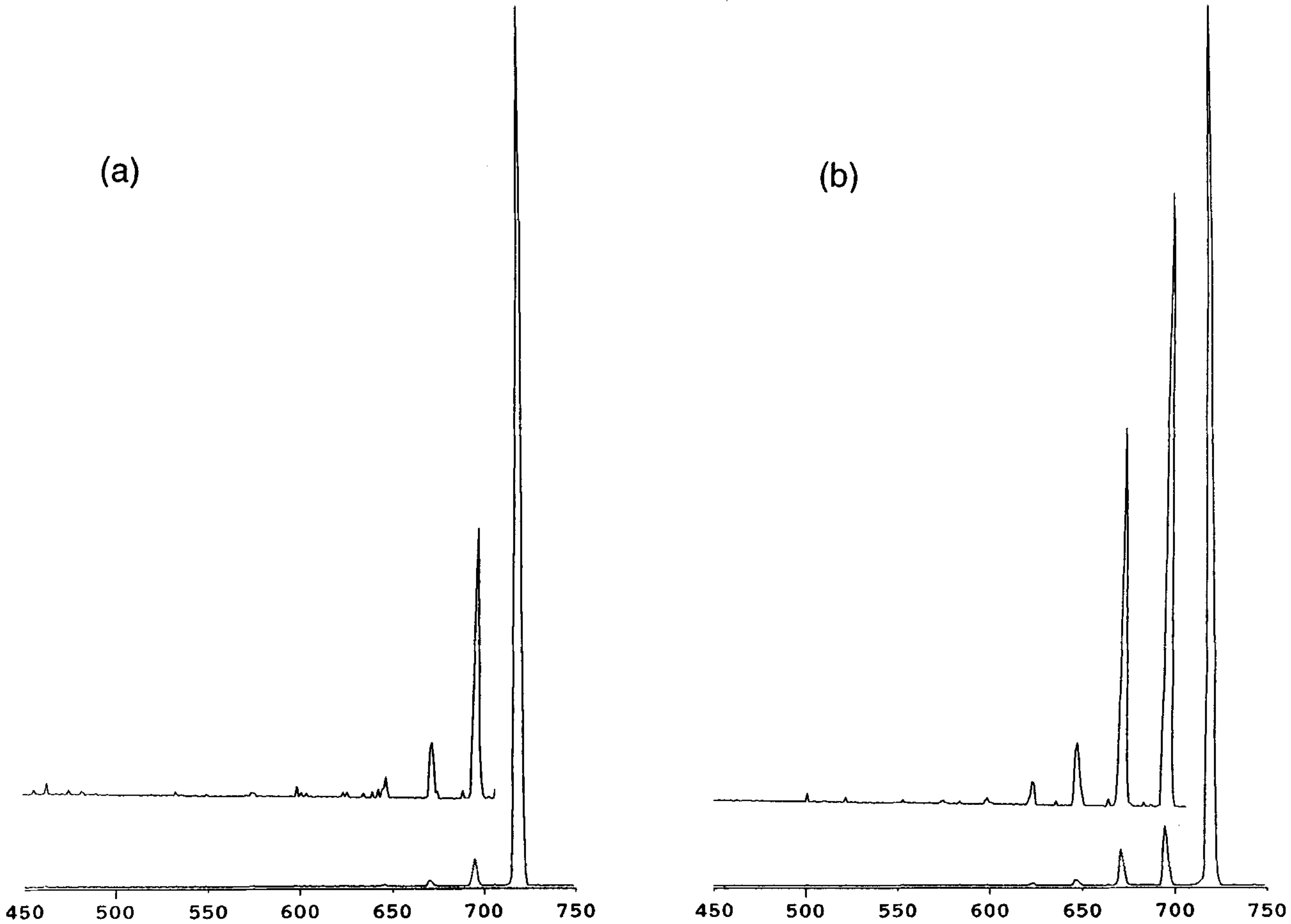

Figure 3. Ion/surface collision spectra obtained by the collision of $C_{60}^{+\cdot}$ at (a) 125 eV and (b) 160 eV collision energies with a surface prepared from 2-(perfluorooctyl)-ethanethiol on vapor-deposited gold.

would fragment at somewhat lower SID energies than in the Whetten[15] or Hertel[36,37] experiments (ions in the latter study probably have internal energies intermediate between Whetten's study and our study). However, the direct comparison of spectra obtained on two different surfaces (Fig. 1, where ions are formed in the same way) indicates that initial internal energy cannot explain the significant differences between the results. If initial internal energy were the main factor involved, both spectra would show significant fragmentation. Unfortunately, it is difficult at this point to estimate the amount of energy deposited into $C_{60}^{+\cdot}$ or C_{60}^{2+} upon collisions with the fluorinated surface because of uncertainties in the initial amount of internal energy present in the ions formed by thermal desorption/electron ionization and uncertainty regarding the energy requirements for fragmentation by loss of C_2. Application of simple RRKM theory[59,60] to our data suggests that either the effective number of oscillators is much lower than $3n-6$ (about one half, 90–100) or that the percentage of translational-to-internal energy conversion for C_{60} is higher for the fluorinated surface than usually reported. Regardless of the exact numbers involved, it is clear that more extensive fragmentation occurs upon collision of C_{60}^{2+} with the fluorinated surface than with alkanethiolate surfaces.

Several explanations are consistent with the greater extent of fragmentation of projectiles that collide with the fluorinated surface as compared with the alkanethiolate surface. Two relatively straightforward physical descriptions can be offered. F is larger in mass than H, which may cause a greater momentum transfer, e.g., for collisions with the carbon of C_{60}^{2+}.[17,19,53,54] Moreover, the greater rigidity of the fluorinated alkanethiol surface ('hard wall' rather than a 'soft mattress')[53] may lead to a smaller uptake of energy by the fluorinated surface compared with the alkanethiolate surface. The greater rigidity of the fluorinated surface can be attributed to enhanced repulsion between the more polar CF dipoles than between the less effective CH dipoles. The Massey parameter, the time of interaction between the incoming projectile and the surface compared with the period of motion being excited, might also be important. A more compressible surface should lead to a longer interaction or excitation time and greater transfer of vibrational energy to the surface. The greater electron density or partial negative charge of the fluorinated surface will result in a repulsive portion of the ion/surface interaction potential that rises more rapidly, and at shorter distances, than the potential surface associated with interaction between the ion and the alkanethiol surface. The interaction time at the fluorinated surface might, therefore, be lower than at the alkanethiolate surface, decreasing the extent of neutralization and resulting in greater electronic perturbation and higher energy deposition. Additional experiments, with a number of different projectile ions and surface types, are required to determine which of the above explanations, if any, most accurately describes the difference in energy deposition between fluorocarbon and hydrocarbon surfaces.

EXPERIMENTAL

The experimental set-up has been described.[16] Two Extrel (Pittsburgh, PA, USA) 4000u quadrupoles are positioned at 90° to a surface placed to intersect the ion-optical path of the two quadrupoles. For the work presented here, ions were produced by 70 eV electron ionization; the sample was placed in a glass capillary on a heated probe tip (400 °C). The surface can be rotated about the z-axis (Q1 and Q2 in the x–y plane). The surface is positioned at 45–50° relative to the surface normal. The collision energy is varied by increasing the source potential relative to the surface potential; to transmit ions past the surface without collision, the potential difference is held at approximately 0 eV. The resolution and sensitivity in this experiment were insufficient to resolve spacing of the C_{13} isotope peak because of the limited volatility of C_{60} and the 400 °C temperature limit of our solids probe.

The C_{60} was synthesized by standard procedures at the Naval Research Laboratory. The alkane thiols were purchased from Aldrich (Milwaukee, WI, USA; 99%). The perdeuterated thiol was synthesized from the corresponding alkyl bromide ($C_{20}D_{41}Br$, Cambridge Isotope Laboratories, Woburn, MA, USA; 97% D) and thiourea by a standard procedure.[60] The fluorinated thiol was prepared from the appropriate iodide ($CF_3(CF_2)_7CH_2CH_2I$, Daikin Chemicals, Japan) and thiourea. The vapor-deposited gold surfaces were obtained from Evaporated Metal Films (Ithaca, NY, USA). The surfaces are 17/32″ × 11/16″ (0.5 mm silica base) and have an underlayer (50 Å) of either titanium or chromium that is covered with 1000 Å vapor-deposited gold. The surfaces were rinsed repeatedly in methanol followed by oxygen plasma cleaning for 15 min. The surfaces were immediately immersed in a 1 mM solution of a given thiol solution and allowed to react for a minimum of 20 h.

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