Surface-Induced Dissociation of Small Carbon Cluster Negative Ions (C_n^-, $n = 5-12$): Correlation between the Dissociation Patterns and Stability of Fragment Ion−Neutral Pairs

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We report detailed study of surface-induced dissociation (SID) of small carbon cluster negative ions (C_n^-, $n = 5-12$) in collision with Si substrates. Fragment mass spectra have been observed in the collision energy range of 0−10 eV/atom. Neutral C_3 loss occurred at collision energies lower than 2 eV/ atom. In the medium energy range (2−6 eV/atom), a marked even−odd difference in the dissociation has been observed: even fragment ions were predominantly generated from incident odd clusters, whereas both even and odd fragment ions from incident even clusters. These results are qualitatively in good agreement with the formation energies of fragment ion−neutral pairs calculated using the experimentally determined binding energies of ions and neutrals. At elevated collision energies (6−10 eV /atom), further fragmentation and electron detachment from fragment ions occurred and smaller cluster ions with even *n* were preferentially generated.

Introduction

Structures and stabilities of small carbon clusters have been subjects of experimental and theoretical works since the discovery of the even−odd intensity alternation of the cluster ions formed in a discharge source in the 1940s.[1] Early experiments concerned intensity variations of the ions and the neutrals produced by heating,[2] spark discharge,[3] and direct laser vaporization of graphite.[4] Quantitative evaluation of the stabilities of the neutral clusters was made by Drowart et al.[2] They estimated average binding energies in $C_1 - C_5$ by observing the temperature dependencies of partial pressures of these species. Attempts to estimate binding energies in ionic clusters have been hindered by the thermal nonequilibrium nature of the ion formation processes. It is rather recent that the binding energies have been estimated by Pargellis.[5]

Alternative ways to evaluate stabilities of clusters are gas-phase dissociation experiments. One can obtain information on dissociation energies and dissociation cross sections and “magic fragments” of clusters through photoinduced fragmentation (PIF).[6,7] Collision induced dissociation (CID) gives similar information on thermally activated dissociations.[8,9] For carbon clusters ($n < 20$), it has been found that the loss of neutral C_3 is the dominant dissociation path for both positive and negative parent ions.[10−13]

Another method, surface-induced dissociation (SID), has been introduced by Whetten et al. for mass-selected cluster ions in the early 1990s[14,15] to investigate cluster-solid interactions. Concerning carbon clusters, they have studied collisions of the negative ions (C_n^-, $n = 5-50$) with Si, gold, and highly oriented pyrolytic graphite substrates.[16] They found that fragmentations occur after the cluster ions are scattered from the surfaces and that preferential fragment paths differ depending on the structures of the incident cluster ions (chains, rings, polycyclic, or cage structures). For the small clusters ($n = 5-17$), it has been revealed that clusters fragment by losing neutral C_3 at low collision energies as in PIF and CID experiments. It was also proposed that stepwise evaporation of carbon atoms follows the C_3 loss at higher collision energies.

McElvany has reported neutral C_2 and C_5 losses as well as the C_3 loss at low collision energies (10−20 eV) in CID of C_n^- with xenon.[13] This leads to an idea that, in SID, an incident ion would also decay by the C_2 and C_5 losses more easily than the loss of a carbon atom from a fragment ion, if the dissociation occurs from the hot parent ions initially scattered intact as pointed out in ref 16. However, such dissociation paths have not been mentioned in the literature. Moriwaki et al. have studied electron detachment from C_n^- in collision with a MoS_2 surface.[17] Although they implied the C_5 loss from parent C_9^- in their report, it is not clear if such thermal processes found in CID are also important in SID.

As illustrated in the above examples, it is still not well understood what happens when a small C_n^- gains internal energies higher than those needed for the C_3 loss by surface impacts. Detailed studies on collision energy dependence of the fragmentation patterns are crucial to clarify the problem.

We report here the collision energy dependence of SID of small C_n^-($n = 5-12$) clusters on Si surfaces. Mass spectra of scattered ions showed clear difference in fragmentation patterns of even and odd incident clusters. The fragmentation patterns at medium collision energies (2−6 eV/atom) were reasonably explained by the formation energies of fragment ion−neutral pairs evaluated by using published data.[5] The results give evidence that the dominant fragmentation paths in this energy range are losses of clusters with up to several carbon atoms.

Experimental Section

Figure 1 shows the experimental setup for the present study. Carbon cluster anions were produced by the laser vaporization method:[18] second harmonics of Nd:YAG laser (Spectra Physics GCR-12, 4−10mJ/pulse) was focused on a graphite rod (Tokai

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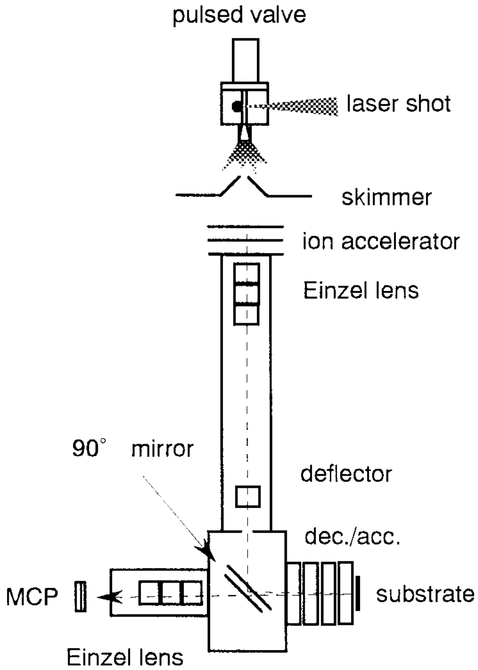

Figure 1. Schematic diagram of the experimental setup.

Carbon: purity >99.99%) and evaporated species were entrained in a pulsed He flow from a solenoid valve (General Valve series 9) and expanded into vacuum. The stagnation pressure was 7 atm. The mass distribution of cluster ions was almost identical to the published one.[17] Higher laser intensity resulted in the population enhancement of smaller clusters. Collision experiments were performed by means of an equipment similar to the one developed by Bernhardt et al.[19] Negative ions were extracted to a drift tube by the Wiley−McLaren's ion accelerator [20] and mass selected by a 90° ion mirror [21] operated in a pulsed manner. The size-selected cluster ions were decelerated and allowed to collide with a Si wafer with a native oxide layer on the surface. Scattered negative ions and electrons were then extracted back by the electric field with which incident ions were decelerated. These ions were focused by an Einzel lens to a tandem microchannel plate detector. Signals from the detector were recorded on a fast digital oscilloscope (Lecroy 7200A). The flight length of the scattered species was about 30 cm. Trajectory simulations of ions for designing the system were performed by the SIMION 3D version 6.0 software package.[22] The collision energy was varied by changing bias voltages on the Si substrate. The width of the collision energy spread was 40 eV (fwhm). Because of this energy spread, some of the ions with low kinetic energies do not collide with the surface but are reflected by the deceleration field. In this paper, collision energy (Ecol) stands for the mean kinetic energy of the colliding ions, i.e., kinetic energy averaged over the distribution. The experiment was carried out for untreated substrates at room temperature. The base pressure in the scattering chamber was 1×10^{-7} Torr.

Results and Discussion

Figures 2a and 2b show representative mass spectra of the ions for collisions of C_{10}^- and C_{11}^-, respectively, with Si. At low collision energies (<2 eV /atom), C_{n-3}^- fragment ions were observed as in the previous works.[16,17] The C_3 loss is the dissociation path which was predominantly observed in CID [12,13] and PIF [10,11] of small positive and negative carbon clusters. These observations are consistent with theoretical works on the

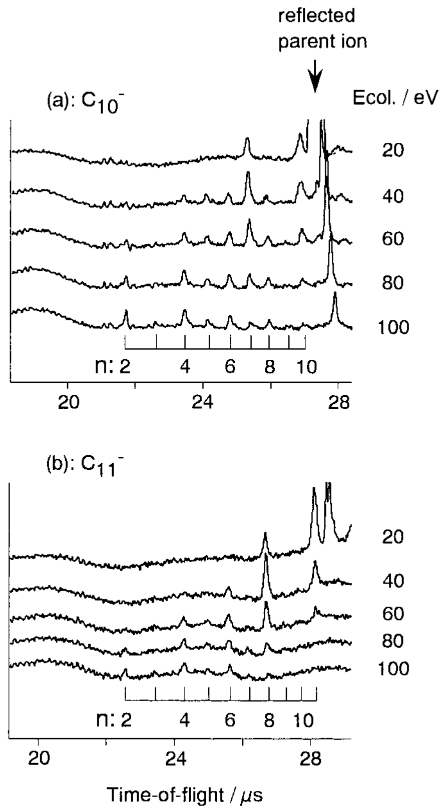

Figure 2. Time-of-flight spectra of ions generated in collisions of (a) C_{10}^- and (b) C_{11}^- with Si surfaces. Mass peaks around 28 μs in (a) are of stray ions (see ref 30). Peaks of emitted electrons are not shown.

ions, which show that the C_3 loss requires ≈1 eV less energy for fragmentation than next probable channels.[23,24]

At elevated collision energies (2−6 eV/atom), mass peaks of ions due to other dissociation paths showed up. As is clearly seen in the figures, even fragments (C_8^-, C_6^-, and C_4^-) were predominantly observed for C_{11}^-, while even (C_8^-, C_6^-, and C_4^-) and odd fragments (C_5^- and C_7^-) appeared with comparable intensities for C_{10}^-. Similar characteristics of the dissociation patterns were found for all incident even and odd parent ions studied in this work: for incident ions with odd n, even fragment ions were dominant in this energy range; on the other hand, both even and odd fragments were observed for incident cluster ions with even n. Figure 3 summarizes the fragment ion intensities for incident $C_n^-(n = 5-12)$ at various collision energies in three-dimensional histograms.

It has been proved in both experimental and theoretical works that even cluster negative ions are more stable than adjacent ones with odd n.[5,25] On the other hand, odd neutral clusters are more stable than adjacent even neutrals for $n = 2-10$.[2,23,26,27] Thus, it is expected that an odd parent negative ion preferably fragment to an even negative ion and an odd neutral (a stable pair). On the contrary, even parents cannot produce such a stable pair, since they fragment to an even (odd) ion and an even (odd) neutral combinations as far as single dissociation is concerned. This therefore seems to be responsible for the observed difference in the dissociation patterns. To substantiate this point, relative pair formation energies of fragment ions and neutral counterparts (ΔEf) in the dissociations of incident C_{10}^- and C_{11}^- were estimated and shown as a function of the size of fragment ions in Figure 4. ΔEf means the energy difference between the formation energy of each pair and that of $C_{n-3}^- + C_3$. We added published binding energies of a negative ion and the neutral counterpart and subtracted the sum from that of $C_{n-3}^- + C_3$.[5,28]

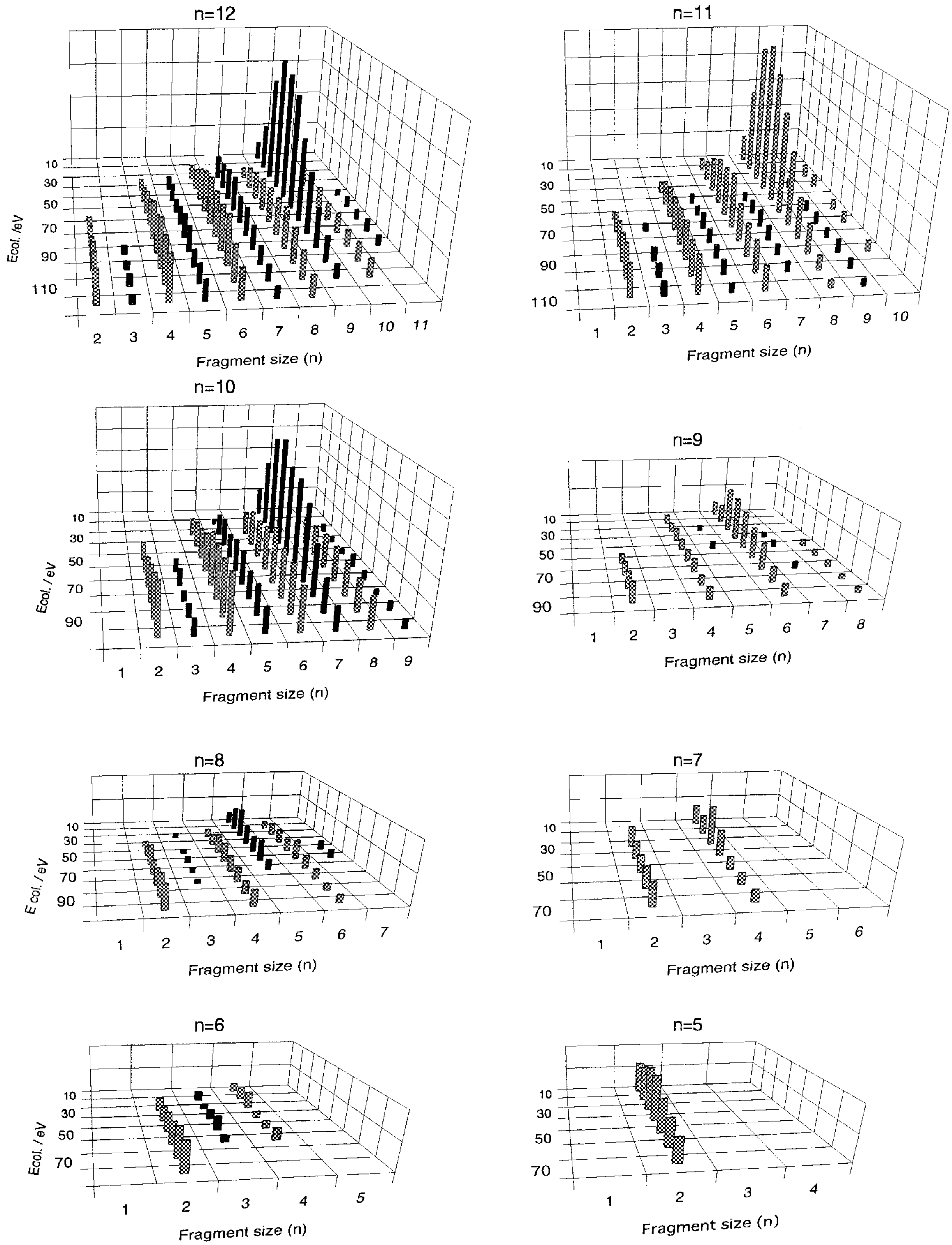

Figure 3. Three-dimensional histograms of the SID fragments for incident even (left column) and odd (right column) *n* carbon cluster negative ions at various collision energies. Solid and shaded bars indicate odd and even fragments, respectively.

This value corresponds to the difference between the energy needed for each fragmentation and that for C_3 loss. Figure 4 shows that, for C_{10}^- and C_{11}^-, C_3 neutral losses are the most energetically favored paths, which is consistent with the present experiment and the published works.[11,13,16,17] What is remarkable in the figure is that ΔEf shows marked even−odd alternation for parent C_{11}^-: fragmentations to generate pairs of even negative ions and odd neutrals require less energies. On the other hand, the variation of ΔEf is rather smooth for parent C_{10}^- except for the C_3 loss fragment. Similar differences can be seen for all even and odd parent clusters ions with $n = 5-12$, which coincides well with the observed mass distributions in the medium collision energy range shown in Figure 3. This consistence suggests that, in this energy range, single dissocia-

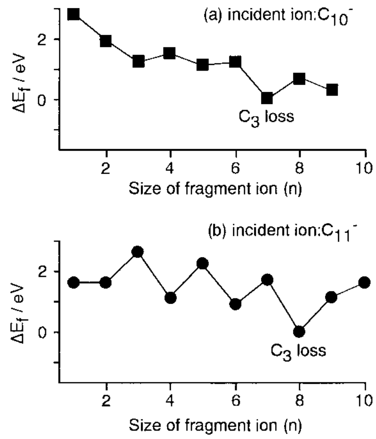

Figure 4. Relative formation energies of fragment ions and neutral counterparts (ΔEf) for (a) incident C_{10}^- (■) and (b) C_{11}^- (●) plotted versus the sizes of the fragment ions. They were calculated using the data in ref 5. See the text.

tions to lose clusters with up to several carbon atoms dominates over the successive evaporation of carbon atoms proposed in ref 16.

It is interesting to note that similar even−odd alternation is expected for SID patterns of C_n^+. For the positive ions, odd clusters are more stable than adjacent even clusters. ΔEf values of fragment positive ion−neutral pairs were estimated in the same manner as we did for parent negative ions, using the binding energies derived by theoretical calculations.[23] The variations of ΔEf of the fragment pairs showed difference between even and odd parent ions: even−odd alternations were seen for incident odd cluster ions, while the variations were rather smooth for incident even clusters except for the C_3 loss fragments. Note that the correlation between the variations of ΔEf and n is reversed from that of the negative ions. For the C_3 loss, ΔEf was smallest for both even and odd parents, which is completely consistent with PIF results as pointed out in ref 23. However, the correlations between ΔEf values and the PIF patterns were not clear for other fragmentation paths. In SID experiment, internal energies deposited on parent ions are much more easily varied than in PIF. Thus, fragmentation patterns observed in SID experiments are expected to be better correlated with ΔEf at certain collision energies as shown in the present work. We are planning to work on SID of positive ions to clarify this point.

One obvious discrepancy between the observed mass distribution and ΔEf is that the intensities of C_{n-1}^- fragments were small for all the parent ions studied. For example, the $C_9^- + C$ fragment pair was estimated to be the most stable pair except for $C_7^- + C_3$. However, the intensity of C_9^- ion was smaller than the other smaller ions for the C_{10}^- incidence. Similarly, C_{n-1}^- fragment peaks are not apparent in the results of previous SID,[16] CID [13] and PIF experiments.[11] In general, charge delocalization effect makes a pair of a small neutral and a large negative ion more stable, which is indeed reflected in the overall decreasing trend of ΔEf with fragment ion size in Figure 4.We do not have a reasonable explanation for this discrepancy between the experimental data and ΔEf values. Kinetic aspects of the dissociation processes may have to be taken into account.

At higher collision energies (6−10 eV/atom), fragment cluster distributions were dominated by smaller masses and even n fragments were predominant. These findings are consistent with the previous experiment.[16] C_3 loss fragments become less intense than others. This result apparently suggests that further fragmentations start to occur in this energy region. Negative cluster ions with even n have higher electron affinities in $n < 10$.[29] Thus, we consider that sequential losses from fragment ions and electron detachment preferentially from energized odd negative fragments result in these trends.

Summary

In this paper we have reported detailed study of SID of small carbon cluster negative ions (C_n^-, $n = 5-12$) on Si. Distinct difference in SID behaviors between even and odd parent ions were observed at collision energies of 2−6 eV/atom. This result can be explained by ΔEf, the relative pair formation energies of fragment ions and neutral counterparts, and suggests that losses of clusters containing one to six carbon atoms from parent ions are important. At elevated collision energies (6−10 eV /atom), further dissociation and electron detachment from fragments are promoted and, as a result, smaller even cluster ions become dominant species in the mass spectra.

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formation processes, binding energies estimated for neutral and ionic carbon clusters produced in a variety of sources such as evaporation, sputtering, and laser ablation were in excellent agreement.

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(30) We apply a pulsed voltage on the 90° ion mirror to select cluster ions with a single size. Since the width of the pulse is adjusted to be the same as (or a little shorter than) drift times of the ions in the mirror to completely exclude other species, the voltage is turned off before a part of the ions go out of the mirror. As a result, these ions exit from the mirror with lower kinetic energies than they had before going into it. They can be detected by the MCP detector after they are reflected by the deceleration field. Such signals are usually detected as broad rises of baselines; however, they sometimes look like mass peaks when initial beam intensities are high. These signals are clearly separated from the reflected parent ions though it is not apparent in the figure.