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Correlation between multiple ionization and fragmentation of C_{60} in 2-MeV Si^{2+} collisions: Evidence for fragmentation induced by internal excitation

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Fragment ions from C_{60} induced by 2 MeV ($v=1.7$ a.u.) Si^{2+} impacts are measured in coincidence with the number distributions of secondary electrons under conditions of single-electron loss and single-electron capture collisions. Multifragmentation, leading to disintegration of cage structure, is found to occur at surprisingly low charge states of $r \simeq 3$. Also, we find that mass distributions of fragment ions are nearly the same for loss and capture collisions provided that the number of electrons ejected, due to electronic energy deposition from an incident ion, are the same. Present results indicate evidently that the internal excitation, rather than the charge state r of transiently formed prefragmented parent ions $C_{60}{}^{r+**}$, plays the essential role in C_{60} fragmentation in fast heavy ion collisions.

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Collision-induced ionization and fragmentation of C_{60} has been the subject of intensive theoretical and experimental studies recently (see Ref. [1] and references therein). Leading motivation of study is that microscopic understanding of these fundamental collision processes is important in basic collision physics and in various applied fields involving polyatomic particles, like fullerenes, lying between atoms and solids. Particular effort has been devoted to elucidation of the role of excitation manners (electronic or vibrational) in C_{60}-fragmentation process using various incident ions and velocities [2–6]. Apart from direct vibrational excitation taking place predominantly in low velocity collisions, two other possible mechanisms might be responsible for C_{60} fragmentation. One is Coulomb explosion from transiently formed highly ionized parent ions and the other is fragmentation from highly excited ions with a sufficiently high amount of internal energy [7]. In collisions of slow highly charged ions (SHCI), such as 300 keV ($v=0.3$ a.u.) Xe^{30+}, the amount of initial charge state (r) plays an important role in fragmentation of $C_{60}{}^{r+}$ ($r=3-9$) [8]. This is reasonably understandable because the internal excitation energy may be low in such SHCI collisions where multiple electron capture is the predominant mechanism leading to production of highly charged $C_{60}{}^{r+}$ ions [8–10]. On the other hand, in collisions of MeV-energy heavy ions where the electronic energy loss is dominant, greater importance of the internal excitation is suggested [11]. Except for these works, however, little is known about the relative importance between transient initial charge states and internal energy of prefragmented parent ions ($C_{60}{}^{r+**}$).

In this work, we provide more direct verification of the relative importance of the internal energy in fast heavy ion collisions. Fragment ions from C_{60} were measured in coincidence with the number (n_e) of emitted electrons and with the charge state (q_f) of outgoing projectile particles using 2.0 MeV ($v=1.7$ a.u.) Si^{2+} incident ions. The measurements were performed for single-electron ($1e$) -capture ($q_f=1$) and $1e$-loss ($q_f=3$) collisions. This triple coincidence measurement provides detailed fragmentation profiles as a function of the charge states of prefragmented $C_{60}{}^{r+}$ parent ions, enabling us to examine the role of initial charge state r in fragmentation processes. It is noted that the present technique is similar to that used in SHCI experiments by Martin *et al.* [12].

The experiment was carried out using a 1.7 MV tandem Cockcroft-Walton accelerator of Kyoto University. Besides our newly developed detector of secondary electrons and an electrostatic charge selector for outgoing projectiles, the rest of experimental apparatuses such as the collision chamber and the time-of-flight (TOF) spectrometer are similar to those described previously [13], and only an essential outline is given below. A well collimated beam of 2.0 MeV Si^{2+} was incident on a target of effusive molecular C_{60} beam produced by sublimation of high-purity (99.98%) powder at 550 °C. A base pressure of the target chamber was kept below 1×10^{-6} Pa. Outgoing projectile ions from the collision chamber were charge selected by electrostatically and detected by a movable semiconductor detector. Product ions from C_{60} were extracted by an electric field of 615 V/cm perpendicular to the incident beam axis and detected by a two-stage multichannel-plate with a front voltage of −4.6 kV. Secondary electrons were extracted to the opposite direction of the product ions and detected by a semiconductor detector (active area=150 mm^2) biased at +30 kV. A pulse height spectrum from the detector provides a n_e distribution, since simultaneous detection of n_e electrons results in a total energy deposition of $30n_e$ keV to the detector [14,15].

A typical example of TOF-n_e coincidence spectra is shown in Fig. 1 obtained for $1e$-loss collisions ($Si^{2+} \rightarrow Si^{3+}$). Vertical and horizontal axes are the time-of-flight of product ions and the pulse height of electrons, respectively. Projection of this two-dimensional spectrum onto these axes provides, respectively, a total TOF and a total n_e spectrum, as demonstrated in the figure. The partial n_e spectrum for any

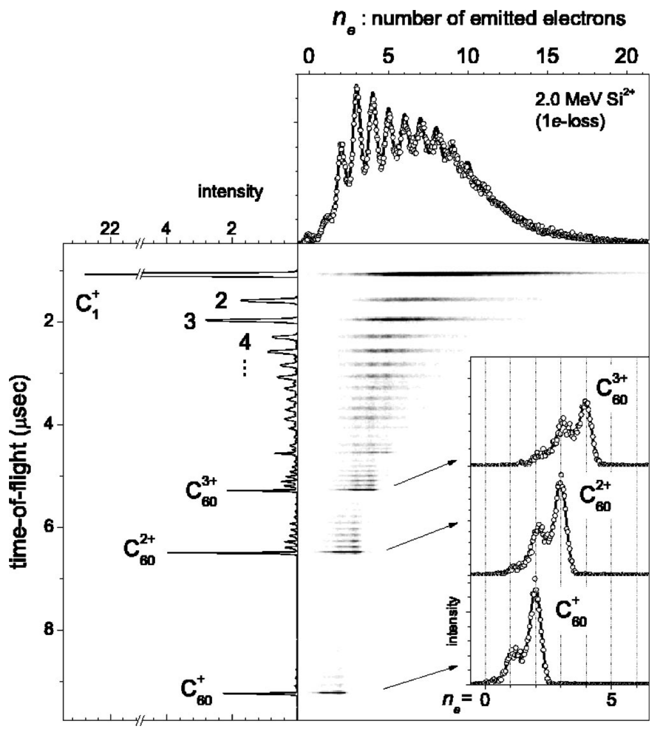

FIG. 1. TOF-n_e coincidence spectrum obtained for single-electron loss collisions of 2 MeV Si^{2+} projectiles. Partial distributions for $C_{60}{}^{r+}$ $(r=1,2,3)$ are shown in the inset.

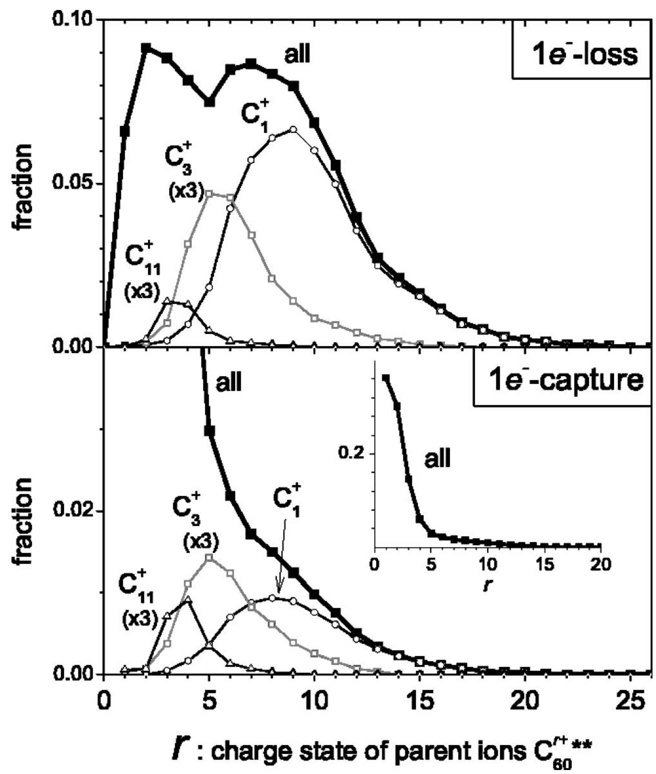

FIG. 2. Electron number (n_e) distributions for $C_n{}^+$ $(n=1,3,11)$ as a function of r. Total distributions (closed squares) over all products ions are normalized to unity.

desired product ion can be obtained from the corresponding TOF region.

As the simplest cases, n_e spectra for parent ions $C_{60}{}^{r+}$ $(r=1-3)$ are depicted in the inset of Fig. 1. The principal peak in each $C_{60}{}^{r+}$-spectrum appears at the expected position of $n_e=r+1$, implying that the electron lost from a Si^{2+} ion is safely detected as well as the r electrons from a $C_{60}{}^{r+}$ ion. Spectator peaks observed in lower side of the principal peaks are known to originate from electron backscattering at the detector surface, depositing a part of the impacting energy (30 keV) into the detector [14,15]. Taking account of this backscattering effect, observed spectra were reproduced almost perfectly as shown by solid lines calculated using constant fitting parameters for the backscattering probability (0.17) and the backscattering K factor (0.6). Note that these fitting parameters are nearly equivalent to published data [14]. Also we note that the electron-collection efficiency of the present experiment was estimated to be about 0.94.

Using these fitting parameters, n_e distributions for individual fragment ions were deduced accurately. Results for $C_n{}^+$ ($n=1,3$, and 11) are presented in Fig. 2 together with the total distributions obtained by the sum of all product ions. Data are plotted as a function of r instead of n_e using the relationship $r=n_e-1$ for loss and $r=n_e+1$ for capture collisions. The partial distribution shows clearly that the average charge state of prefragmented parent ions increases significantly with decreasing cluster size n. The total distributions for loss and capture collisions are considerably different from each other. This is due to different contributions from intact parent ions from which only a few electrons are ejected. We find, therefore, that the 1e-capture process accompanies preferential production of intact parent ions, as observed in our previous TOF-q_f coincidence experiments [16]. It implies that the 1e-capture process is dominated by distant or soft collisions even in our velocity region. As an important experimental finding, however, it should be pointed out that the partial distributions for small fragment ions reveal nearly the same shape for loss and capture collisions. For instance, mean values of r for $C_1{}^+$ were about 9.8 and 9.3 for 1e-loss and 1e-capture collisions, respectively. It suggests that a small fragment ion of a fixed cluster size is created in nearly the same impact-parameter collisions for both loss and capture collisions.

As the most important data obtained in this work, fragment ion distributions produced at fixed charge states of prefragmented parent ions are presented in Fig. 3. First, the figure shows clearly that multifragmentation starts to occur at surprisingly low charge states of $r\simeq 3$ in loss collisions and $r\simeq 4$ in capture ones. It is well known that C_{60} is substantially strong against Coulomb repulsion force [17–20]. Actually, in recent experiments using an infrared femtosecond laser, fullerene ions $C_{60}{}^{r+}$ with charge states as high as $r=12$ are observed [17]. Martin *et al.* reported that, in SHCI experiments (300 keV Xe^{30+}), $C_{60}{}^{r+}$ $(r<5)$ ions scarcely disintegrate and, e.g., 99.7% of $C_{60}{}^{3+}$ ions remain intact [8]. They reported that the production of highly charged $C_{60}{}^{r+}$ ions is dominated by distant collisions of impact parameters larger than 32 a.u. for $r\leqslant 9$ [8]. Note impact parameters measured from the center of C_{60}. Consequently, the internal excitation energy of C_{60} is expected to be low in such distant collisions. By contrast, in our case, $C_{60}{}^{3+}$ ions remain intact

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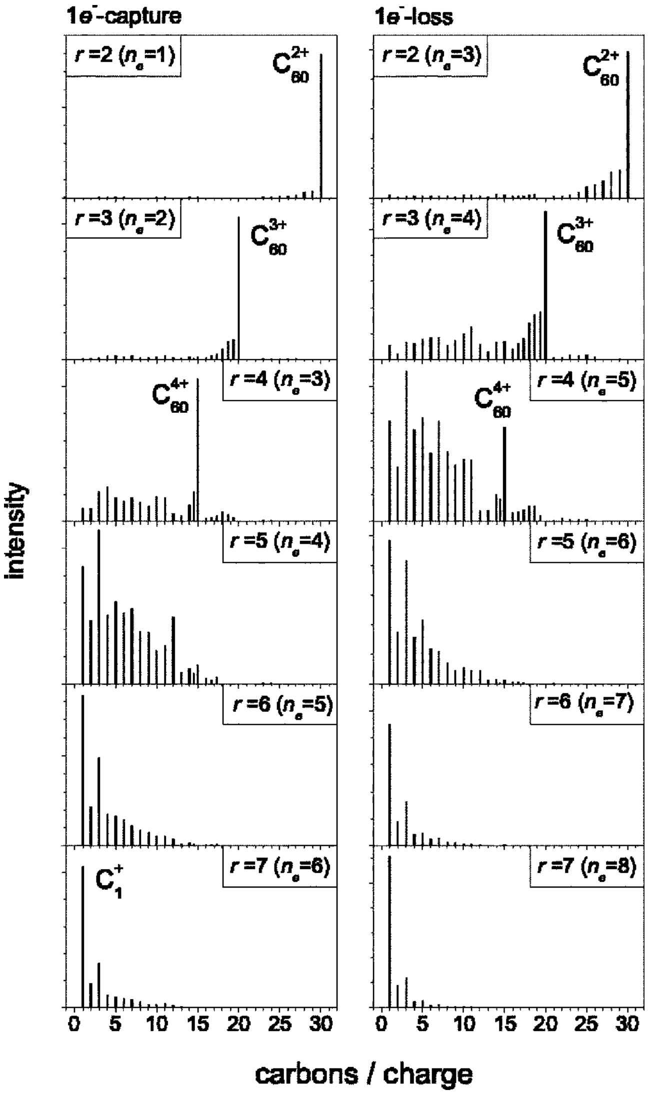

FIG. 3. Correlated production of fragment ions at fixed charge states (r=2–7) of prefragmented parent ions $C_{60}{}^{r+}$.

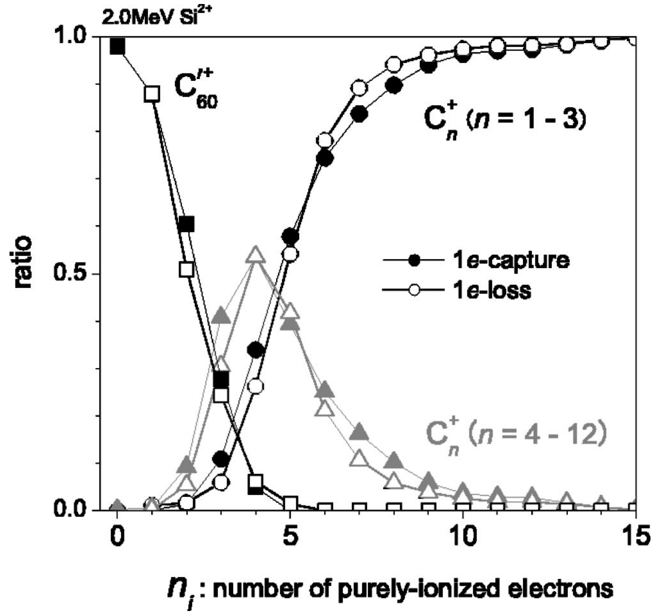

FIG. 4. Intensity ratios of $C_{60}{}^{r+}$ (squares), sum of $C_n{}^+$ (n =4–12) (triangles), and sum of $C_n{}^+$ (n=1–3) (circles) for 1e-loss (open) and 1e-capture (closed) collisions.

only by 27% for 1e-loss collisions (61% for capture ones). The different results obtained in SHCI and our fast ion collisions may be attributed solely to a difference of internal excitation energy deposited into a C_{60} molecule. This is because, in our lowly charged fast ions, $C_{60}{}^{r+}$ ions are likely produced in closer collisions receiving a larger amount of excitation energy compared to SHCI collisions.

Second, there exists remarkable resemblance between (r)-spectra in 1e-loss and ($r+1$)-spectra in 1e-capture collisions; compare the spectra of, e.g., $r=4$ in loss with $r=5$ in capture collisions. On the contrary, distribution profiles at the same r are significantly different from each other. It is noted that one of $r+1$ electrons in 1e-capture collisions is captured into a projectile ion and the rest r electrons are purely ejected via ionization processes taking place simultaneously. Note that the simultaneous events among inelastic processes such as charge-changing, excitation, and ionization are typically observed in collisions of fast heavy ions with many-electron atomic targets [21]. Denoting the number of this pure ejection by n_i, the present result indicates that overall multifragmentation profiles are governed by the amount of n_i, rather than the apparent charge state r itself. This one-electron-shift of fragmentation profile is more explicitly depicted in Fig. 4 as a function of n_i, where $n_i=r$ in 1e-loss and $n_i=r-1$ in 1e-capture collisions. Here, we plot relative intensities of intact parent ions $C_{60}{}^{r+}$, medium sized fragments $\Sigma_{n=4}^{12} C_n{}^+$ and the first three smallest ions $\Sigma_{n=1}^{3} C_n{}^+$ with respect to total intensities of all product ions. Plotted data for loss and capture collisions are found to coincide fairly well with each other.

It is known that the electronic energy deposition E_e is shared between excitation and ionization of target electrons with a certain partition rate [22,23]. Thus, it may be possible to estimate the amount of internal excitation energy E_{int} from the values of n_i. For this estimation, however, exact values of partition rates are required. So far, no experimental and theoretical work has been reported referring to such partition rates for fullerene particles. For other collision systems, two theoretical papers are available for 0.2–10^4 keV $H^+ + H_2O$ [23] and 1.4 MeV/amu U^{32+}+Ne [22]. According to these studies, the partition rate to the excitation branch is about 0.2 at the present incident velocity [23]. As for the ionization branch with a rate of 0.8, it is further divided into two branches of kinetic energies of ejected electrons and their ionization potentials. The partition rate spent for ionization potentials E_p is about 0.25 [22]. If we simply use these partition rates, we obtain $E_p(=E_e \times 0.8 \times 0.25) \simeq E_{int}(=E_e \times 0.2)$. The present value of n_i is related to E_p by

$$E_p \geqslant \sum_{r=1}^{n_i} I_r, \tag{1}$$

where the rth ionization potential I_r of C_{60} may be calculated by $I_r(\text{eV})=3.77+3.82r$ [24]. The internal energy E_{int}

estimated in this way are 53 eV, 103 eV, and 168 eV for n_i=4, 6 and 8, respectively, at which multifragmentation occurs strongly (Fig. 3). According to the maximum entropy calculations made by Campbell *et al.* [7], the multifragmentation starts at $E_{int} \simeq 85$ eV and complete disintegration into smaller fragment ions occurs beyond 200 eV. Present rough estimations compare fairly well with these theoretical predictions, although present values seem to be not high enough to induce such strong multifragmentation as observed experimentally. In order to obtain more reliable values of E_{int} from n_i, accurate partition rates in the present collision system are needed. From the close connection between E_{int} and n_i, it follows convincingly that the internal energy of ${C_{60}}^{r+}$ in 1*e* loss may be essentially equivalent to that of ${C_{60}}^{(r+1)+}$ in 1*e*-capture collisions, because of the same values of n_i for both cases. Together with the experimental findings of resemblance of fragmentation profiles at the same n_i, it leads us to a conclusion that the fragmentation profile in fast collisions is essentially governed by the internal excitation energy rather than the apparent charge state *r*. For higher charge states ($n_i \sim r > 10$), however, the Coulomb explosion may also become responsible for the fragmentation.

In summary, we performed triple coincidence measurements for TOF, n_e and q_f to study correlated ionization and fragmentation processes of C_{60}. A careful comparison of the fragmentation profiles between 1*e*-loss and 1*e*-capture collisions shows that the C_{60} fragmentation is governed by the number of purely ejected target electrons, implying that the internal excitation energy is more important than the apparent charge state *r* itself in 2-MeV Si^{2+} collisions. It should be addressed, however, that accurate values of energy-partition rates are urgently required to know the role of internal excitation effect more quantitatively.

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