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Correlation between multiple ionization and fragmentation of $\text{C}_2\text{H}_6$ in charge-changing collisions with 580-keV C$^+$

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We investigate correlations between multiple ionization and fragmentation processes of the ethane molecule in collisions with 580-keV C$^+$ ions under single-electron capture and loss conditions. Employing an electron counting technique, we directly obtain number distributions of ionized electrons, which correspond to distributions of multiple ionization probabilities of ethane. In addition, fragmentation patterns as a function of the charge state $r$ of intermediate parent ions $\text{C}_2\text{H}_6^{r+}$ are obtained from coincidence measurements between the time of flight of the product ions and the number of electrons emitted. Fragmentation patterns in the different charge-changing conditions reveal a crucial role of the internal excitation in the fragmentation processes. Also, we provide clear evidence of strong selectivity on the parent charge state for formation of the H$_3^+$ ion, which is exclusively generated through doubly charged parent ions $\text{C}_2\text{H}_6^{2+}$.

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1. INTRODUCTION

Ion-impact ionization of molecules followed by subsequent dissociation is the first-stage fundamental process in the course of ion-irradiation effects on living cells [1]. In particular, multiple-electron ionization becomes important in collisions of fast heavy ions of MeV energies because the amount of electronic energy deposition becomes large. Unstable multiply charged molecules formed transiently in such collisions generate easily a variety of fragment products and radicals which are known to act as a trigger for complicated physicochemical reactions in the medium. It is also known that secondary electrons of less than a few tens of eV play a significant role in radiation damage of DNA [1–3]. Hence, quantitative information about the probability of multiple ionization and the resulting fragmentation of multiply charged molecular ions is of great importance to achieve fundamental understanding of the underlying mechanisms of radiation effects in matter.

To date, a large number of studies of collision-induced ionization, excitation, and fragmentation of molecules have been performed for isolated gas-phase molecular targets. Owing to recent development of coincidence techniques, correlation between fragment ions can be studied in detail for small-size molecules consisting of a few atoms [4]. In those measurements, distributions of multiple ionization are derived by summing up the charge states of the fragment ions detected together in each collision event [5,6]. As for larger molecules composed by many atoms, however, probabilities of the complete detection of several fragment ions becomes extremely low due to finite detection efficiency, limiting the possibility of determining the degree of multiple ionization of parent molecules formed transiently before fragmentation. Actually, experimental investigations of molecules—hydrocarbon molecules, for instance—are limited only to measurements of fragment ions and not more [7–23]. Little is known about the details of fragmentation processes from highly charged large molecules.

On the contrary, an electron counting method using a semiconductor detector is capable of direct deducing of the degree of multiple ionization. The method was originally developed to measure the number distributions of secondary electrons from a solid surface by ion impacts [24,25], and then applied to studies of fragmentation of isolated C$_{60}$ molecules in the gas phase [26–29]. For gas-phase molecular targets, the number of secondary electrons $n_e$ gives straightforwardly the degree of multiple ionization of the target molecules. Furthermore, by measuring simultaneously the time of flight (TOF) of fragment ions, correlation between charge states of parent ions prior to fragmentation and fragmentation patterns can be deduced correctly. It should be stressed again that this coincidence technique has a great advantage over conventional methods particularly for highly multiple ionization of large molecules because reliable estimation of the intermediate charge state becomes practically impossible with limited detection efficiency of product ions from highly charged large molecules. We can expect that detailed studies on fragmentation processes of large molecular ions as a function of their charge states will shed new light on the characteristic decay mechanisms of highly charged molecular ions.

In this paper, we employed this technique to investigate fragmentation processes of the ethane molecule (C$_2$H$_6$) bombarded by 580-keV C$^+$ ions. It should be noted that this energy range and the charge state are more closely relevant to interaction in the Bragg peak region, compared to frequently investigated conditions like few keV or higher charge states [30–32]. We measured the distribution of multiple ionization of C$_2$H$_6$ molecules and the correlation between fragment ions and charge states of their parent ions. The measurements were performed under conditions of single-electron (1e) capture and loss collisions. It is noted that the fragmentation of ethane has been studied previously by means of conventional coincidence methods using electron impacts [33–36] and strong laser fields [37–42]. In particular, the H$_3^+$ production from hydrocarbon molecules has been known since early work in mass spectrometry [43] and still attracts considerable attention as one of the simplest examples of chemical reactions involving intramolecular bond rearrangement [7,12,38,39,42,44,45] and in interstellar chemistry [46]. In electron impacts and photoionization experiments, the H$_3^+$ ions are observed in binary fragmentation of
doubly charged parent ions, i.e., C$_2$H$_6$$^{2+}$ → H$_3^+$ + C$_2$H$_3^+$, using conventional coincidence methods [38–41,43]. Here, we examine more systematically the relationship between the charge state $r$ and the H$_3^+$ production in the present ion-impact experiments in which parent molecules can be highly ionized with $r > 2$. In the following section, an outline of our experimental apparatus and method is described. In Sec. III, detailed discussion is given for fragment ion distributions in TOF spectra, secondary electron distributions equivalent to the distribution of multiple ionization, and correlation between fragment ions and charge states of their parent ions. Conclusions are given in Sec. IV.

II. EXPERIMENT

The experiment was performed at a 1.7-MV tandem accelerator facility of Quantum Science and Engineering Center, Kyoto University. Figure 1 shows a schematic diagram of the experimental setup consisting of our previous two different detection systems for secondary electrons using a solid-state detector [28,29] and for product ions using a position-sensitive detector [47]. A beam of 580-keV C$^+$ ions was collimated with two sets of four-jaw slits, then charge purified by a magnetic charge selector just before a collision chamber, and crossed with a gas jet target of C$_2$H$_6$. A typical gas pressure in the collision chamber during measurements was about 6 × 10$^{-4}$ Pa. Note that the velocity of the projectile ions is 1.4 a.u., at which an interaction with a target molecule is completed in the order of 0.1 fs.

Product ions, including fragment ions and intact ions of C$_2$H$_6$ molecules generated in collisions, were extracted perpendicular to the projectile-beam axis by an electric field with two mesh electrodes separated by 10 mm from each other. Ions were detected by a microchannel plate (MCP) detector in conjunction with a position-sensitive delay line detector (DLD). The total detection efficiency is limited by transmission probabilities of grid meshes of the extract electrodes and efficiency at the MCP detector and DLD. The detection probability of each product ion was estimated to be about 0.2 in the present system. The mass-to-charge ratio $m/q$ of product ions was obtained with a TOF spectrometer operated under a Wiley-McLaren spatial focusing condition [48]. Pulse signals from the DLD were recorded with a digital storage oscilloscope (LeCroy, WavePro7000). The TOF and the incident position on the MCP detector of each product ion were obtained by analyzing the timing of the pulse signals.

Outgoing projectile ions with different charge states $q_f$ were separated by an electrostatic deflector and detected by a movable semiconductor detector (SSD$_p$). In this work, two charge-changing collision conditions corresponding to 1e capture ($q_f = 0$) and 1e loss ($q_f = 2$) were selected. Collision events occurring under a specific charge-changing condition were obtained from SSD$_p$ signals as the trigger timing for the TOF measurements.

Secondary electrons emitted in collisions were extracted to the opposite direction of the product ions and detected by a semiconductor detector (SSD$_e$) on a potential at +25 kV. Each electron hits the detector with an energy of 25 keV, and thus the total energy of 25$n_e$ keV is deposited into the SSD$_e$ when $n_e$ electrons are emitted in a single collision. Since the semiconductor detector provides signals with pulse heights proportional to the deposited energy, distributions of $n_e$ are derived by analyzing pulse-height distributions (or energy spectra) of SSD$_e$ signals. The pulse height of the SSD$_e$ signal was recorded by a multichannel analyzer (MCA) in coincidence with the DLD signals of the product ions for each collision event. When no electron is detected during the gate of the MCA opening in coincidence with ion detection, the MCA records an amplitude of an electric signal fluctuating around the zero-volt baseline. Coincidence measurements between the TOF of ions and the pulse height of SSD$_e$ signals provide information on correlation between fragment ions and the charge state of parent ions prior to fragmentation.

To deduce the number distributions correctly, the $n_e$ spectra need to be analyzed by a fitting procedure based on the model which takes account of the electron loss due to finite collection efficiency and the electron backscattering at the detector surface [24]. Parameters used in the fitting procedure, including collection efficiency of the secondary electrons and so on, were evaluated from a separate experiment using an argon gas target. When an Ar$^+$ ion is detected in a 1e capture collision, the true number of $n_e$ is uniquely determined to be $(r − 1)$ since one electron among $r$ electrons is transferred to the projectile ion. By analyzing $n_e$ distributions in coincidence with Ar$^+(r = 1−4)$ detections, the collection efficiency was estimated to be about 93%, which is consistent with the transmission rate of the mesh electrode. The other parameters used in the present analysis are basically similar to the previous values evaluated with the C$_{60}$ target [28,29].

III. RESULTS AND DISCUSSION

Figure 2 represents two-dimensional (2D) coincidence maps between product ions and secondary electrons obtained for 1e capture and 1e loss collisions of 580-keV C$^+$ ions with C$_2$H$_6$. The horizontal and vertical axes are the TOF of product ions and the pulse height of SSD$_e$ signals, respectively. The pulse-height distributions are referred to as “$n_e$ spectra” hereafter. As shown in the figure, projection of the coincidence data in 2D maps onto the two axes gives a total TOF spectrum and a total $n_e$ spectrum, respectively. Longitudinally aligned data points of $n_e$ correlated with a specific product ion give the number of electrons emitted in collisions where the specific ion is produced, referred to as a “partial $n_e$ spectrum” in this
paper. Similarly, horizontally aligned data points in a specific region give a partial TOF spectrum for collision events with \( n_e \)-electron emission. These spectra were carefully analyzed by taking account of the electron counting loss and backscattering effect at the detector surface of SSD. [28,29]. The correction procedure of these effects is described in the Sec. III C.

### A. Product ions (total TOF spectra)

The total TOF spectra of product ions are classified into three groups according to the number of constituent carbon atoms as follows: (i) ions which maintain a C-C bond, \( C_2H_n^+(n = 0\text{–}6) \), (ii) ions with a single carbon atom, \( \text{CH}_n^+(n = 0\text{–}3) \), and (iii) hydrogen atomic and molecular ions, \( \text{H}_n^+(n = 1\text{–}3) \). In comparison with the electron-impact experiments [33–36], the present results show higher degrees of fragmentation achieved by large energy transfer induced by fast heavy ion collisions. Intensity distributions show that \( \text{H}^+ \) is the dominant product ion in both 1e capture and loss collisions. Besides \( \text{H}^+, \text{C}_2\text{H}_n^+ \) ions of the group (i) are the second dominant products in both collisions, while C-C bond-broken ions of group (ii) are produced rather strongly in 1e loss collisions. Note that doubly charged \( \text{C}_2\text{H}_2^{2+} \) ions appear at the same TOF positions of singly charged \( \text{CH}_n^+ \) ions. Separation of these spectra is possible because of a large difference of peak widths due to different kinetic energies [40]. Namely, sharp peaks of \( \text{C}_2\text{H}_2^{2+} \) superimpose on broad peaks of C-C bond-broken \( \text{CH}_n^+ \) ions. Careful analysis of peak profiles reveals that the peak intensities of \( \text{C}_2\text{H}_2^{2+} (n = 2, 3) \) are about 10% of those of \( \text{CH}_n^+ \) ions in 1e capture collisions, while such double structures are not seen clearly in 1e loss collisions, indicating smaller fractions of the doubly charged ions.

A typical feature of TOF spectra in group (i) is that the \( \text{C}_2\text{H}_4^+ \) ion is produced most abundantly with intensities much stronger than the intact parent ion \( \text{C}_2\text{H}_6^+ \) and \( \text{C}_2\text{H}_3^+ \) in both charge-changing collisions. The reason is explained by different appearance energies \( (E_{\text{app}}) \) of these ions. According to an experimental study with electron-impact ionization [49], the \( E_{\text{app}} \) of \( \text{C}_2\text{H}_6^+ \), \( \text{C}_2\text{H}_3^+ + \text{H} \), and \( \text{C}_2\text{H}_3^+ \) are 11.46, 12.7, and 11.90 eV, respectively. Namely, the difference of \( E_{\text{app}}(\text{C}_2\text{H}_6^+) \) and \( E_{\text{app}}(\text{C}_2\text{H}_3^+ + \text{H}_2) \) is only 0.44 eV, which basically corresponds to the energy barrier for dissociation into \( \text{C}_2\text{H}_2^+ + \text{H}_2 \). Thus, excited parent ions \( \text{C}_2\text{H}_5^+ \), produced initially in collisions, can easily dissociate into \( \text{C}_2\text{H}_4^+ \) ions by releasing a neutral \( \text{H}_2 \) molecule as a result of relaxation of internal excitation energies deposited in collisions. In addition, \( E_{\text{app}}(\text{C}_2\text{H}_3^+ + \text{H}_2) \) is higher than \( E_{\text{app}}(\text{C}_2\text{H}_3^+ + \text{H}) \) by about 0.8 eV. Thus, \( \text{C}_2\text{H}_6^+ \) decays to \( \text{C}_2\text{H}_4^+ + \text{H}_2 \) as a preferential pathway rather than to \( \text{C}_2\text{H}_2^+ + \text{H} \).

One can see that the intensity of \( \text{CH}_3^+ \) ions produced via C-C bond breakings are much stronger in 1e loss than 1e capture collisions. Also, the fragment ions with smaller number of hydrogen atoms \( n \) become stronger in 1e loss collisions; see, e.g., the \( \text{C}_4^+ \) ion as the dominant product ion in group (ii). These features imply evidently higher energy deposition in electron loss collisions than in capture collisions, reflecting the fact that electron loss occurs predominantly at smaller impact parameters while electron capture can take place even in distant collisions. Discussion is given in more detail in the following subsections.

### B. Multiple ionization (total \( n_e \) spectra)

In Fig. 2, the \( n_e \) spectra (i.e., pulse-height distributions of SSD signals) show a series of separated peaks with a constant interval corresponding to 25 keV. Simultaneous detection of \( n_e \) electrons generates a pulse signal with a height corresponding to 25\( n_e \) keV. A peak as “\( n_e = 0 \)” around 0 keV...
in the 1e capture condition is due to pure single-electron capture collisions without additional ionization. The width of this peak reflects fluctuation of the baseline mainly due to thermal noise of the semiconductor detector. As observed clearly in the figure, such events of \( n_e = 0 \) are dominant and other peaks decrease steeply with increasing \( n_e \) in 1e capture collisions. In 1e loss collisions, the \( n_e \) distribution appears to take a maximum around \( n_e = 2 \) or 3. Figure 3(a) shows our fitting results by solid lines which reproduce perfectly the experimental \( n_e \) spectra (black dots) in both electron capture and loss collisions. Histograms depicted in Fig. 3(b) are the true number distributions deduced by this fitting procedure. Here, the data are plotted as a function of the charge state \( r \) of parent ions \( \text{C}_2\text{H}_6^{r+} \).

In our collision system, a target molecule \( \text{C}_2\text{H}_6 \) is highly ionized and excited transiently to unstable intermediate states and decays via subsequent fragmentation. Here, we define \( n_i \) as the number of "pure ionization" in which \( n_i \) electrons of a \( \text{C}_2\text{H}_6 \) molecule are released into vacuum without being captured by projectile ions. In terms of \( n_i \) and \( n_e \), the values of \( r \) can be expressed as \( r = n_i - n_e + 1 \). Thus, the charge-changing condition. In such situations, it is impossible to deduce realistic distributions shown in Fig. 3(b), from the coincidence data of product ions.

C. Correlation between product ions and multiple ionization (TOF-\( n_e \) coincidence)

A series of \( r \) distributions of intermediate parent ions \( \text{C}_2\text{H}_6^{r+} \) correlates with specific product ions (labeled by \( i \)) that were obtained accurately by analyzing the vertically aligned coincidence data of product ions. As mentioned before, for small molecular targets with a few constituent atoms, the charge state \( r \) may be deduced solely from coincidence data of product ions without knowing the number of secondary electrons. However, for larger molecules, the simultaneous detection of all the fragment ions becomes very hard due to limited detection efficiency of the ion detector. In the present measurement, the detected coincidence count of more than three ions was only a few out of 100 000 collision events recorded in each charge-changing condition. In such situations, it is impossible to deduce realistic distributions shown in Fig. 3(b), from the coincidence data of product ions.

2.6 while it is only 0.8 for 1e capture collisions. Higher multiple ionization in 1e loss collisions is consistent with higher multifragmentation discussed in Sec. III A.

Before proceeding to the discussion of correlation between multiple ionization and fragmentation, we emphasize again that the simultaneous measurement of the number of secondary electrons is essential (indispensable) to determine \( r \) distributions accurately. As mentioned before, for small molecular targets with a few constituent atoms, the charge state \( r \) may be deduced solely from coincidence data of product ions without knowing the number of secondary electrons. This is because the fragmentation of such a molecule involves only a few fragment ions at a maximum and all of them may be detected with a reasonably high probability. However, for larger molecules, the simultaneous detection of all the fragment ions becomes very hard due to limited detection efficiency of the ion detector. In the present measurement, the detected coincidence count of more than three ions was only a few out of 100 000 collision events recorded in each charge-changing condition. In such situations, it is impossible to deduce realistic distributions shown in Fig. 3(b), from the coincidence data of product ions.
methods, we stress here that this strong charge selectivity of 
H$_3^+$ formation pathway from C$_2$H$_6$$^{2+}$ is proved quantitatively
in the present work. Correlation data among product ions
reveal that H$_3^+$ ions are produced together with C$_2$H$_3^+$ and
C$_2$H$_4^+$ ions, being consistent with previous photoionization
experiments [43]. The branching ratio of pathways from
C$_2$H$_6$$^{2+}$ to either H$_3^+$ + C$_2$H$_3^+$ or H$_3^+$ + C$_2$H$_4^+$ (+H) is
obtained as 8:2 for both 1e capture and loss conditions. This
branching ratio is nearly equivalent to the photoionization
result of 85:15 reported in [43]. It means that the probability of
neutral H emission accompanying the H$_3^+$ formation is
less dependent on the ionization mechanisms. This is
somewhat amazing because internal excited states of C$_2$H$_6$$^{2+}$
are expected to be largely different from one another in
1e capture, 1e loss, and photoionization. Nevertheless, the
almost equivalent branching ratios between ion impact and
photoionization imply that the H$_3^+$ ion is generated only from
specific excited states of C$_2$H$_6$$^{2+}$ irrespective of the means of
ionization.

Likewise, the r-distribution peaking at r = 2 for H$_2^+$
production indicates obviously that H$_2^+$ may also be produced
predominantly through a preferential reaction pathway from
doubly charged parent ions. An open question is the origin
of this preferential charge selectivity of r = 2, unlike other
fragment ion species although parent molecules are ionized
widely from singly up to r ∼ 6.

In order to demonstrate more explicitly the difference
between 1e capture and loss collisions, the fragmentation
patterns at fixed values of r are plotted in Figs. 6(a) and 6(b),
where we plotted the intensities $I_i(i)$ of ions denoted by i from
fixed charge states r of intermediate parent ions C$_2$H$_6$**,

$$I_i(i) = W_i(r) I(i).$$

where $I(i)$ is the total intensity of the product ion i derived
from the total TOF spectra shown in Fig. 2. For comparison,
distributions of fragment ions produced by 200-eV electron
impacts [33] via C$_2$H$_6$$^{++}$ and C$_2$H$_6$$^{2+}$ parents are also shown
as r = 1 and 2, respectively, in Fig. 6(c). It should be noted that
these distributions were obtained by analyzing coincidence
data of fragment ions without electron counting measurements.
This is available for the electron-impact experiments because
multiple ionization is less important in their experiment;
double ionization is only 8% and triple ionization is negligibly
small in total ionization.

Firstly, the $I_i(i)$ distribution at r = 1 in 1e capture condi-
tions, as shown in Fig. 6(a) corresponding to the pure 1e
capture process without additional ionization, shows C$_2$H$_{n+}$
as the dominant product ion. It implies that the detachment
of neutral H and/or H$_2$ is the main dissociation pathway from
C$_2$H$_6$$^{n+}$. At r = 2, C$_2$H$_{n+}$ ions are suppressed strongly while
fragment ions of CH$_{n+}$ and H$_2^n+$ get produced prominently.
Here, it is interesting to point out that the intensity distributions
at r = 1 and 2 for 1e capture conditions surprisingly resemble
those in Fig. 6(c) obtained by electron impacts [33]. This
means that electronic excitation accompanied by 1e capture
collisions is comparable to those with electron-impact ion-
ization. Obviously, such gentle electron capture collisions
correspond mainly to distant collisions.

With increasing charge state r, the bond-breaking processes
proceed further. The intensity distributions of fragment ions
with different n among CH$_{n+}$(n = 0−3) and C$_2$H$_{n+}$(n = 0−6) exhibit large shift toward smaller n with increasing r,
resulting in the predominant production of H$_2^+$, C$_3^+$, and C$_2^+$. In
contrast, we realize that the intensity ratio between groups (i) and (ii) does not change largely even at \( r \sim 3 \) and 4. In order to see this feature more explicitly, the intensities integrated over fragment ions in each group are plotted in Fig. 7 as a function of the parent charge state \( r \) in the 1e capture and loss conditions.

Next, we compare the intensity distributions \( I_r(i) \) between 1e capture and loss conditions. We can see here an important role of the internal energy in determining fragmentation patterns. Smaller fragment ions produced from C-H and C-C bond breakings appear rather prominently in 1e loss collisions at any \( r \) in comparison with those in 1e capture collisions. This high fragmentation in loss collisions means that higher internal excitation is induced in loss collisions than capture collisions even at the same charge state \( r \). Furthermore, one can notice immediately the nearly equivalent fragmentation patterns between \( r = 3, 4 \) in 1e capture and \( r = 2, 3 \) in 1e loss collisions; \( I_{r+1}(i)\text{cap} \approx I_r(i)\text{loss} \). This reminds us of the relationships \( n_i = r - 1 \) and \( n_i = r \) for 1e capture and loss collisions, respectively. Namely, the fragmentation patterns in 1e charge-changing collisions are nearly the same when the numbers of pure ionization \( n_i \) are the same irrespective of the different values of \( r \). It implies that the internal excitation energy, rather than the charge state \( r \), governs the degree of fragmentation. This can be understood in the following way. Following a statistical model [50], the value of \( n_i \) is a good measure of the amount of internal excitation energy because the total electronic energy deposition from a projectile ion is shared between ionization and internal excitation with certain partition rates, e.g., 80% for ionization and 20% for excitation at the present incident velocity [50,51]. In addition, it is considered that 1e capture itself by an incident ion does not accompany greatly the extra excitation of the residual electronic system of a target molecule. Thus, once \( n_i \) is the same, the internal excitation energy of the molecule is

![Graph showing intensity distributions for 1e capture, 1e loss, and 200-eV electron collisions.](image)

**FIG. 7.** (Color online) Fractions of integrated intensities of (i) \( \Sigma C_2H_n^+ \) \((n = 0 - 6)\), (ii) \( \Sigma CH_n^+ \) \((n = 0 - 3)\), and (iii) \( \Sigma H_n^+ \) \((n = 1 - 3)\) in the total intensities of product ions as a function of the parent charge state \( r \) in the 1e capture and loss conditions.
expected to be the same order of magnitude irrespective of either electron capture or loss collisions, resulting in the equivalent fragmentation patterns. It should be pointed out that this remarkable feature of \( n_i \), instead of \( r_i \), was observed in C\(_{60}\) fragmentation experiments using 2-MeV Si\(^{2+}\) ions \cite{28}. It is somewhat surprising that such a simple statistical property seems to hold not only for C\(_{60}\) but also for C\(_2\)H\(_6\) composed of only eight atoms.

IV. SUMMARY

Multiple ionization and subsequent dissociation of C\(_2\)H\(_6\)\(^{r++}\) produced by 580-keV C\(^{+}\) impacts have been investigated by a comprehensive coincidence method. Namely, simultaneous measurements of fragment ions and secondary electrons produced from gas-phase C\(_2\)H\(_6\) molecules were performed in coincidence with the final projectile charge states under 1e capture and 1e loss conditions. With this method, we could directly obtain the multiple ionization probabilities in the specific charge-changing conditions. Consequently, we achieved detailed investigation of the fragmentation of highly charged molecules with specific charge states. Results obtained in this work are as follows.

The mean numbers of additional pure ionization \( n_i \) accompanying 1e capture and loss collisions were obtained as 0.8 and 2.6, respectively. Fragmentation patterns in total TOF spectra indicate higher energy deposition in 1e loss than 1e capture collisions, implying smaller impact-parameter collisions in 1e loss collisions. Comparison of partial TOF spectra at fixed charge states \( r \) also exhibits a higher degree of multifragmentation in 1e loss than 1e capture collisions. However, if we compare the spectra at the same number of \( n_i \), both spectra are found to coincide fairly well with each other. This fact implies evidently from statistical arguments that the internal energy plays a decisive role for determination of the fragmentation patterns of ethane. We found that the C-C bond survives at a certain probability even in highly multiple ionization up to \( r \sim 5 \) or 6, indicating that the C-C bond in highly charged C\(_2\)H\(_6\)\(^{r++}\) ions can remain until the ions become a singly charged state via prompt desorption of protons. Finally, we proved quantitatively that H\(^{3+}\) ions are generated only from specific excited states of doubly charged parent ions.

As demonstrated in this work for ethane molecules, the present coincidence technique is a promising powerful tool to make detailed investigation of multiple ionization of larger molecules such as biomolecules. Multiple ionization and charge-specific reaction processes of highly charged polyatomic molecular ions will be studied in detail in the future.

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