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Charge Transfer and Metastable Ion Dissociation of Multiply Charged Molecular Cations Observed by Using Reflectron Time-of-Flight Mass Spectrometry

Akihiro Kitashoji[†],^[a] Kosei Kitagawa[†],^[a] Akimasa Fujihara,^[b] and Tomoyuki Yatsuhashi^{*[a]}

Abstract: A multiply charged molecule expands the range of a mass window and is utilized as a precursor to provide rich sequence coverage; however, reflectron time-of-flight mass spectrometer has not been well applied to the product ion analysis of multiply charged precursor ions. Here, we demonstrate that the range of the mass-to-charge ratio of measurable product ions is limited in the cases of multiply charged precursor ions. We choose C_6F_6 as a model molecule to investigate the reactions of multiply charged molecular cations formed in intense femtosecond laser fields. Measurements of the time-of-flight spectrum of C_6F_6 by changing the potential applied to the reflectron, combined with simulation of the ion trajectory, can identify the species detected behind the reflectron as the neutral species and/or ions formed by the collisional charge transfer. Moreover, the metastable ion dissociations of doubly and triply charged C_6F_6 are identified. The detection of product ions in this manner can diminish interference by the precursor ion. Moreover, it does not need precursor ion separation before product ion analysis. These advantages would expand the capability of mass spectrometry to obtain information about metastable ion dissociation of multiply charged species.

1. Introduction

Increasing demands for the precise structure determination of medically, biologically, and/or chemically important macromolecules highlight mass spectrometry as one of the leading tools applicable to these substances.^[1] A variety of ionization sources, site-specific fragmentation methods, and analytical instruments have been developed.^[2] Tandem mass spectrometry (MS/MS) has been widely used to obtain structure information, in which a particular precursor ion is selected by the first MS, precursor ion fragmentation is completed, and product ions are analyzed by the second MS.^[1,3] Depending on the methods by which the precursor ion is activated, a suitable MS/MS have been used.^[4–9] Conventionally, time-of-flight mass spectrometer (TOF-MS) with an ion mirror, namely reflectron

TOF-MS (refTOF-MS) combined with matrix assisted laser desorption/ionization (MALDI) has commonly been used for the analysis of product ions of macromolecules due to its high precursor ion selectivity, high mass-resolving power, high transmittance, and unlimited mass range.^[1] However, it should be mentioned that refTOF-MS has not been well utilized for the product ion analysis of multiply charged precursor ions, although great successes have been achieved in those of singly charged precursor ions. In this article, we show that particular product ions emerged from multiply charged precursor ion are not detected under the condition for the analysis of the product ions of singly charged precursor ion. We use multiply charged molecular cations (MMCs),^[10–12] which are prepared in abundance by sequential tunnel ionization in intense femtosecond laser fields,^[13–15] to show the behavior of product ions that transmit the reflectron in refTOF-MS. Hexafluorobenzene (C_6F_6), which has small mass and simple dissociation channels, is chosen as a model molecule to analyze charge transfer reactions and metastable ion dissociations of MMCs.

2. Results and Discussion

2.1. Revisiting the Working Principle of refTOF-MS.

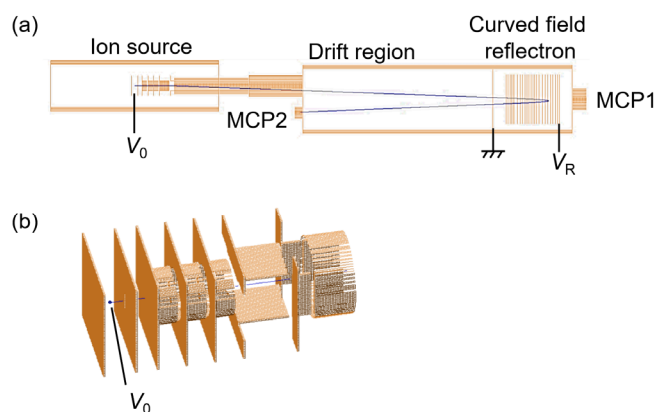


Figure 1. (a) Schematic of refTOF-MS. (b) Details of the electrodes in the ion source. The blue line indicates the trajectory of $C_6F_6^{2+}$ ($V_0 = 2740$ V, $V_R = 3865$ V).

Schematic of Wiley–McLaren time-of-flight mass spectrometer equipped with an offset curved field reflectron^[16–18] and micro-channel plate detectors (MCP1, MCP2) is shown in Figure 1. Ion

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packet of MMCs is prepared by focusing femtosecond laser pulses in an ion source. Here, we revisit the working principle of reTOF-MS for the analysis of product ions emerged from MMCs. Supposing that MMC with mass m_1 (in kg units) and charge z_1 (in C units) is formed at potential V_0 (in V units) in the ion source, the energy conservation law gives

$$z_1 V_0 = \frac{1}{2} m_1 v^2, \quad (1)$$

where v (in m s^{-1} units) is the velocity of MMC. Once products are formed from a MMC by metastable ion dissociation or charge transfer by the collision with neutral gases in the drift (field-free) region, the precursor MMC and its products have the same velocity v since the kinetic energy releases in the collision and/or fragmentation processes are expected to be smaller than the initial kinetic energy of a precursor ion. It should be emphasized that the consideration of charge is not necessary when we treat singly charged precursor ions, whereas both the mass and charge should be taken into account when the product ions of MMCs enter the reflectron, to which V_R (in V units) is applied. The minimum potential V_R^m (in V units) necessary to reflect the product ion with mass m_2 ($\leq m_1$, in kg unit) and the charge z_2 ($\leq z_1$, in C units) is described by

$$z_2 V_R^m = \frac{1}{2} m_2 v^2. \quad (2)$$

Thus, we obtain

$$V_R^m = \frac{m_2/z_2}{m_1/z_1} V_0. \quad (3)$$

Supposing that z_2 is equal to z_1 , V_R^m should be smaller than or equal to V_0 . Therefore, all product ions are reflected at the potential $V_R = V_0$. However, the product ion can pass through the reflectron with potential V_0 , if m_2/z_2 is larger than m_1/z_1 . Consequently, such product ions cannot be detected under the condition for the analysis of the product ions emerged from a singly charged precursor ion by using the reflectron and MCP2.

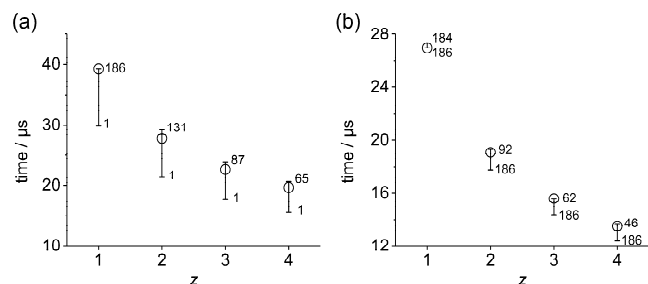


Figure 2. Simulated flight time of the product ion of $C_6F_6^{z+}$ detectable (a) by MCP2 at $V_R = 3865$ V and (b) by MCP1 at $V_R = 2700$ V. Circles indicate the flight time of precursor $C_6F_6^{z+}$. Values beside the bars indicate the m/z of detectable product ions. V_0 is fixed to 2740 V.

Here we calculated the trajectory of product ions to judge whether product ions were detected by MCP2 or not under a constant V_R condition. First, we fixed $V_R = 3865$ V that is optimal voltage for the analysis of product ions emerged from singly charged precursor ion with our reTOF-MS. Figure 2a shows the flight time of the product ion that is reflected by the reflectron followed by the detection with MCP2. It is obvious that the simulated m/z ranges of product ions detectable by MCP2

satisfied the condition derived from eq. (3) ($\frac{m_2/z_2}{m_1/z_1} \leq \frac{V_R}{V_0} = 1.41$). For example, the product ions of $C_6F_6^{2+}$ (m/z 93) with m/z between 1 to 131 ($= 93 \times 1.41$) can be detected. It is emphasized that the range of detectable product ions is narrower for more highly charged precursor ions. For example, the product ions of $C_6F_6^{3+}$ (m/z 62) with m/z 1–87 are detectable by MCP2. At the same time, those with m/z 88–186 passed through the reflectron under the condition of the ordinary use of our reTOF-MS.

Above-mentioned results indicate that we need to apply V_R much higher than V_0 to reflect all product ions of MMC, i.e. widening of the available mass window with MCP2. There is one successful report for the collision-induced dissociation experiment on doubly charged precursor ions. Toyoda and coworkers measured the product ions of doubly protonated bradykinin (m/z 531.1) up to m/z 1100.^[19] In their experiments, the kinetic energy of the precursor ion was 4.5 keV, and the potential of the final electrode at the rear part of the reflectron was maintained at 12 kV. Therefore, their experimental setup satisfied the requirement to observe all possible product ions of doubly charged bradykinin. Product ion analysis might be possible, if appropriate potential is applied to both acceleration and reflectron electrodes. However, such optimization is usually not possible in a commercially available tandem TOF-MS with a reflectron.^[20,21] Moreover, we face the difficulty to satisfy those requirements especially when we analyze the product ions of multiply protonated molecules formed by MALDI, because the typical acceleration voltage used in MALDI is 20 kV to achieve a high detection efficiency of ions with large masses such as proteins. The above-mentioned fact that a part of information about product ions with m/z higher than the m/z of the respective multiply charged precursor ion has been lost, has not well been known, but it is an unavoidable problem when using conventional reTOF-MS. If the information of such missing product ion that passes through the reflectron had been collected, it may have provided additional information helpful for the structure determination.

Thus, we tried to simulate the flight time of the product ions that passed through the reflectron. It is noted that the flight times of the product ions passing through the reflectron are somewhat difficult to simulate because all marker ions, whose m/z is well identified, are reflected at V_R above V_0 ($= 2740$ V). Therefore, we first simulated the flight times of product ions detectable by MCP1 at $V_R = 2700$ V (Figure 2b). Under this condition we can, for example, detect the product ions of $C_6F_6^{3+}$ with m/z 62–186 by MCP1.

2.2. Reflection of Ions Formed in the Ion Source by the Reflectron.

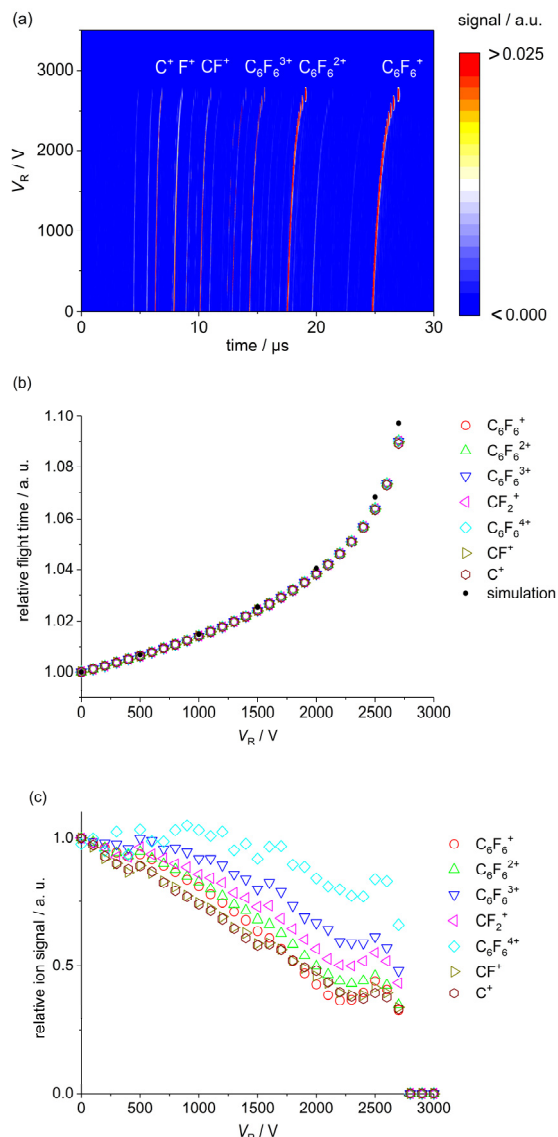


Figure 3. (a) Time-of-flight contour spectrum, (b) relative flight time, and (c) relative signal of representative ions detected behind the reflectron as a function of V_R (100 V step): $C_6F_6^+$ (circles), $C_6F_6^{2+}$ (triangles), $C_6F_6^{3+}$ (inverted triangles), CF_2^+ (left-pointing triangles), $C_6F_6^{4+}$ (diamonds), CF^+ (right-pointing triangles), C^+ (hexagons). Ion signal and flight time are normalized to those obtained at $V_R = 0$ V. Signals of $C_6F_6^{4+}$, $C_6F_6^{2+}$, and $C_6F_6^{3+}$ in (a) are saturated. The time-of-flight spectra measured at several V_R are shown in Figure S1a. The C_6F_6 pressure was 5×10^{-4} Pa. The laser intensity was 5.2×10^{14} W cm^{-2} . (b) includes the results by ion trajectory simulation (dots).

Multiple ionization of gaseous C_6F_6 was carried out by focused femtosecond laser pulses delivered from a 1-kHz-repetition-rate Ti:Sapphire laser (0.8 μ m, 40 fs).^[22] We varied the voltage applied to the reflectron (V_R), while the accelerating potential ($V_0 = 2740$ V, electric fields was 1389 V cm^{-1}) was kept constant. As V_R increased, the signal of ions gradually decreased and the flight times of the ions increased (Figures 3a). The time-of-flight spectra measured at several V_R are shown in Figure S1a. The

relative flight times and relative signal intensity of representative ions as a function of V_R are shown in Figures 3b and 3c, respectively. Here we calculated the flight times of these ions at different V_R by using an ion trajectory simulation program for the present reTOF-MS configuration shown in Figure 1. Relative flight time shifts were independent of ion species and were well simulated, as shown in Figure 3b. The decrease in ion signal was dependent on the ionic species, and all ions showed hump-like feature at around 2500 V. Although we are currently not sure about the origin of such feature, all ions disappeared at the same V_R , which we denote as the disappearance voltage V_R^d . We obtained $V_R^d = V_0$ for the ions shown in Figure 3c. These observations are expected from the working principle of reTOF-MS: the ions that are accelerated at potential V_0 in the ion source are reflected by the reflectron at $V_R = V_0$. Supposing that the kinetic energy release in the formation of product ions is negligible, V_R^d would coincide with V_R^m .

2.3. Neutral Species Formed by Charge-transfer.

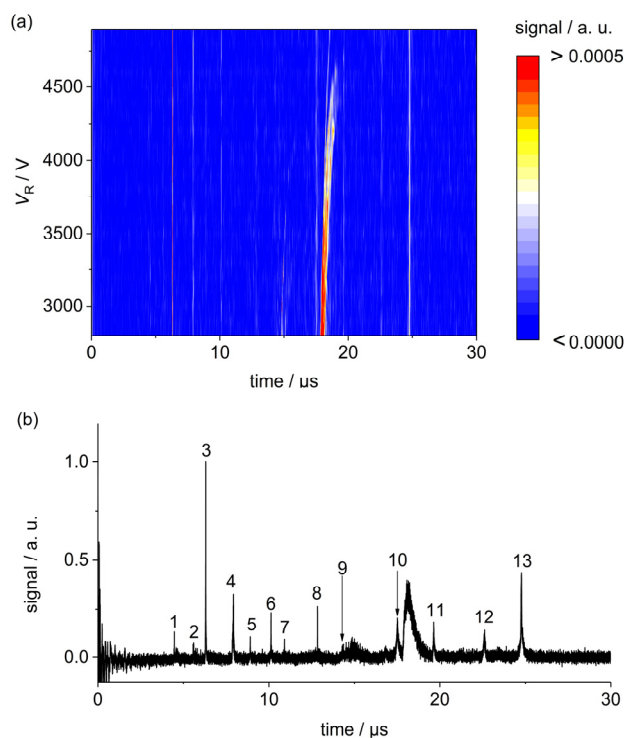


Figure 4. (a) Time-of-flight contour spectrum taken behind the reflectron as a function of V_R (100 V step). The time-of-flight spectra measured at several V_R are shown in Figure S1b. (b) Average of the 22 mass spectra taken behind the reflectron (V_R between 2800 and 4900 V, 100 V step). The peaks denoted as 1 – 13 are the neutral species originated from C^{2+} , F^{2+} , C^+ , F^+ , C_2^+ , CF^+ , C_3^+ , CF_2^+ , $C_6F_6^{3+}$, $C_6F_6^{2+}$, $C_5F_3^+$, $C_5F_5^+$, and $C_6F_6^+$, respectively. The C_6F_6 pressure was 5×10^{-4} Pa. The laser intensity was 5.2×10^{14} W cm^{-2} .

As discussed in 2.1 and examined in 2.2, intact molecular ions and fragment ions formed in the ion source are reflected when the reflectron has the potential equal to or slightly higher

than the acceleration potential V_0 (2740 V in this study). However, some peaks were still observed by MCP1 at V_R above 2800 V (Figures 4a). The time-of-flight spectra measured at several V_R are shown in Figure S1b. These peaks are indistinguishable at first sight under the constant V_R condition, but varying V_R enables us to distinguish neutral species from ionic ones.

Neutral species are definitively identified because both the flight time and signal intensity were independent on V_R . Therefore, mass spectra taken between V_R 2800 and 4900 V were averaged (Figure 4b). This procedure does not alter the position, shape, or intensity of neutral peaks but improves the signal quality. Peaks broaden and appeared at ca. 15 and 18.5 μs by this averaging are not neutral species. Thirteen neutral peaks denoted as 1–13 were clearly identified. The precursor ions of 1–13 were assigned to be C^{2+} , F^{2+} , C^+ , F^+ , C_2^+ , CF^+ , C_3^+ , CF_2^+ , $\text{C}_6\text{F}_6^{3+}$, $\text{C}_6\text{F}_6^{2+}$, C_5F_3^+ , C_5F_5^+ , and C_6F_6^{+} , respectively, based on the coincidence of the flight times between peaks 1–13 and their respective precursor ions measured at $V_R = 0$ V.

Neutral species are originated from the charge transfer between the residual C_6F_6 gas and the fully accelerated precursor ions, which were formed in the ion source. Comparison of the adiabatic ionization energy of C_6F_6 (9.9 eV)^[23] with the recombination energy of cations gives the energetics of the charge transfer.^[24] Here we consider the five largest neutral peaks (3, 4, 6, 8, 13) in Figure 4b. The recombination energies of C^+ , F^+ , CF^+ , CF_2^+ , and C_6F_6^{+} are 11.3, 17.4, 9.1, 11.4, and 9.9 eV, respectively.^[23–26] We can say that the charge transfer to C_6F_6 forming C_6F_6^{+} is an exothermic process for C^+ , F^+ , CF_2^+ , and C_6F_6^{+} since their recombination energies are higher than or equal to the ionization energy of C_6F_6 . In the case of CF^+ , of which charge transfer is endothermic process, dissociative charge transfer might form a neutral species.^[24]

2.4. Product Ions of Doubly and Triply Charged C_6F_6 .

Positively charged species are distinguished from neutral ones by varying V_R . Their flight times are increased by increasing V_R because the cations are decelerated by the potential applied to the reflectron. We classified cationic species into two groups based on their peak shapes. One is relatively sharp peak denoted as A, B, and C, and the other is broad peak denoted as D and E as shown in Figures 5 and S2. Here, we discuss the origin of the first group (peaks A, B, and C) and then of the second group (peaks D and E). Peaks A and B were detected at 14.5 and 14.8 μs at $V_R = 2800$ V (Figures 5a and S2a), respectively, where the product ions of $\text{C}_6\text{F}_6^{3+}$ are expected to appear. Peak C appeared at 17.9 μs at $V_R = 2800$ V (Figures 5b and S2b) and is assigned to the product ion of $\text{C}_6\text{F}_6^{2+}$. In order to characterize these peaks, we measured the signal intensity and flight time as a function of V_R . In contrast to the results shown in Figure 3, V_R^d as well as the relative flight time shifts were differed by cationic species.

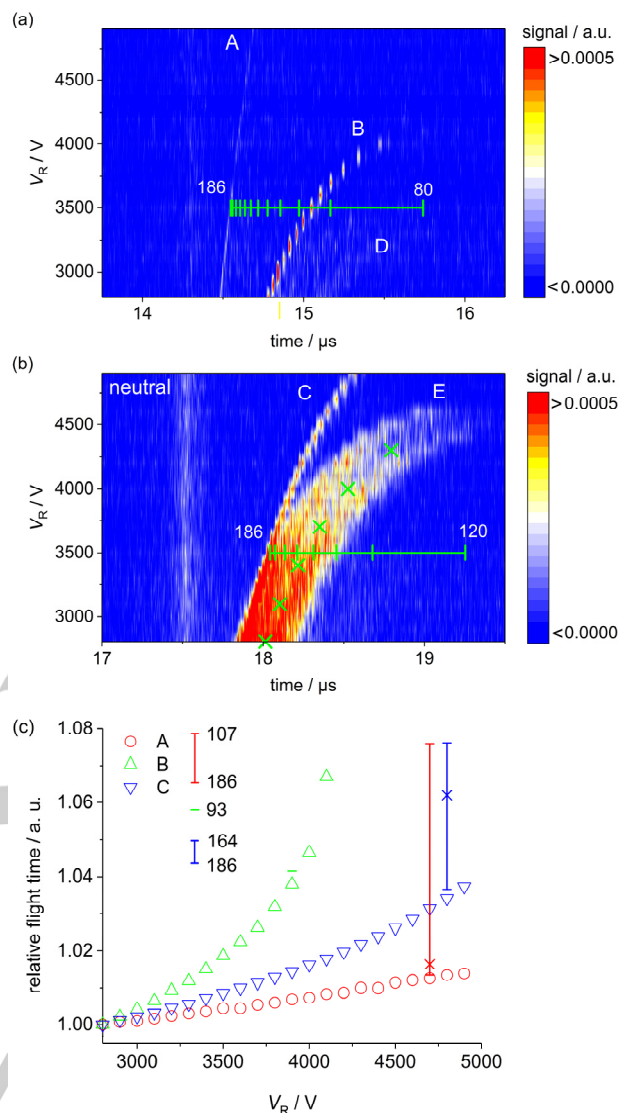


Figure 5. Time-of-flight contour spectra of product ions originating from (a) $\text{C}_6\text{F}_6^{3+}$ and (b) $\text{C}_6\text{F}_6^{2+}$ taken behind the reflectron by varying V_R (100 V step). The m/z scales simulated at $V_R = 3500$ V are shown (a, m/z 80–180 increased by 10 and m/z 186; b, m/z 120–180 increased by 10 and m/z 186). Green crosses in (b) indicate the simulated flight times of the product ion with m/z 155. The time-of-flight spectra measured at several V_R are shown in Figure S2. (c) Relative flight times of product ions A (circles), B (triangles), and C (inverted triangles) detected behind the reflectron as a function of V_R . Flight times were normalized to those obtained at $V_R = 2800$ V. Bars on data A, B, and C show the simulated relative flight time of the product ion with m/z of 107–186, 93, and 164–186, respectively. Crosses on bars indicate the simulated relative flight time of the product ion with m/z 167. The C_6F_6 pressure was 5.0×10^{-4} Pa. The laser intensity was 5.2×10^{14} W cm^{-2} .

First, we estimated m/z of product ions by V_R^d . According to eq. 3, V_R^d provides information about m_2/z_2 and hence m/z of a product ion. V_R^d of B was estimated to be 4090 V, whereas those of A and C were not determined (>4900 V) due to the limitation of our power supply. We can convert V_R^d of the peaks B to m/z 93. In contrast, only the lower limits of m/z for the peaks A (111) and C (166) were obtained. Therefore, we next evaluate m/z by

relative flight time shift. Figure 5c shows relative flight times of the product ions A, B, and C. As V_R increases, the range of detectable product ion becomes narrower, but the separation of unit m/z becomes wider. Thus, the relative flight times evaluated using an ion trajectory simulation at high V_R were compared with those obtained by experiments. The flight time of B was well reproduced by the simulation. The relative flight times of A and C seem to be identical to those simulated for the ion with the largest m/z (186, $C_6F_6^{3+}$). Nevertheless, we need to judge the possibility of the product ion with the second largest m/z as A and/or C. Table S1 shows possible combination of m/z for $C_mF_n^{z+}$ ($m, n = 0-6, z = 1-3, m = n \neq 0$). Based on the m/z (93) evaluated by V_R^d , we can assign peak B to $C_6F_6^{2+}$. According to the data listed in Table S1, the second candidate for the product ions A and C is $C_6F_5^+$ (m/z 167). The simulated relative flight times of $C_6F_5^+$, which are indicated by the crosses in Figure 5c, were well separated from the experimentally obtained ones. Based on V_R^d s and simulations of relative flight time, we assign the peaks A, B, and C to be the charge transfer products $C_6F_6^{3+}$, $C_6F_6^{2+}$, and $C_6F_6^+$, respectively. We propose that m/z determination by using the relative flight time shift is more advantageous than that by using V_R^d in the cases of charge transfer products because the peak position is accurately determined. Consequently, we can use $C_6F_6^{3+}$ as a marker ion to draw m/z scale of the product ions of $C_6F_6^{3+}$ and $C_6F_6^{2+}$. Figures 5a and 5b show the m/z scale of the product ions with (a) m/z 80–186 and (b) m/z 120–186 that pass through the reflectron at $V_R = 3500$ V.

Herein, we consider the broad peaks D and E, which appeared between 14.8 and 15.3 μ s and between 17.9 and 18.2 μ s, respectively, at $V_R = 2800$ V. It is certain that the former peak originates in the product ion of $C_6F_6^{3+}$ and that the latter peak originates in that of $C_6F_6^{2+}$. We can recognize that peak E was separated into bimodal-like broad peaks as V_R increased (Figure 5b). The broadness of a peak might be attributable to the unimolecular decomposition process that occur at different locations and/or to the kinetic energy that is released upon bond dissociation. Since the position of a peak is not accurately determined, we may obtain a more reasonable m/z of a product ion by V_R^d rather than by ion trajectory simulation. Unfortunately, the intensity of broad peak D originating from triply charged C_6F_6 was too low, but we can state that V_R^d is between 3600 and 3800 V corresponding to m/z 81 – 86. We could suggest $C_6F_5^{2+}$ (m/z 83.5) as the most probable candidate listed in Table S1. The broad peak E centered at around 18 μ s at $V_R = 2800$ V disappeared at around 4650 V, which was converted to m/z 158. Based on the m/z evaluated by V_R^d and the established m/z data of fragment ions obtained by electron ionization as well as by the VUV photoionization of C_6F_6 (Table S1), we suggest that the product ion formed by the metastable dissociation of $C_6F_6^{2+}$ is $C_5F_5^+$ (m/z 155).^[27] Flight time simulation also supports this assignment (crosses in Figure 5b). This evaluation would be reasonable because the dominant metastable dissociation process of $C_6F_6^{2+}$, which was formed by a high-energy photon, to $C_5F_5^+$ was confirmed by coincidence spectroscopy, where the kinetic energy release was measured to be 3.9 eV.^[27]

Finally, we should mention that the abundance of ionic species is similar to that of neutral species indicating that the actual yield of product ions formed by metastable ion dissociation is negligible because the detection efficiency of MCP for ionic species is much higher than that for neutral species. These facts reveal that multiply charged C_6F_6 cations produced in femtosecond laser fields are much more stable than that formed by VUV ionization as presented in the previous study.^[22,29]

3. Conclusions

In this work, we propose a method to obtain the information about the product ions of multiply charged precursor ions using a reTOF-MS. Product ions passing through the reflectron are characterized by their disappearance voltage and their relative flight time shifts. The performance of this method was examined by observing the charge transfer reaction of hexafluorobenzene. The triple charge transfer observed for hexafluorobenzene draws further interest as to whether multiple charge transfers occur in a direct or a sequential manner. Moreover, the metastable dissociation of a hexafluorobenzene dication and trication radical was identified. Mass spectrum measurements by changing the potential applied to the reflectron, combined with ion trajectory simulation, suggests alternative avenues to investigate at least the m/z of a product ion of multiply charged precursor ions that is not obtained by the ordinary use of conventional reTOF-MS. Although the mass-resolving power and the sensitivity must be improved for further application, the initial results presented above suggest that detection of products behind the reflectron is a viable alternate product ion detection strategy. Our results further suggest that a new reTOF-MS for multiply charged precursor ions could be constructed by inserting a high-energy filter to reflect precursor ion and fragment ions that are formed in the ion source, and deceleration optics before the reflectron to improve the mass resolution of product ions with minimal modification.

Experimental Section

The experimental details have been described elsewhere.^[28] Briefly, the multiple ionization of hexafluorobenzene and xenon was carried out with a linearly polarized 40-fs pulse centered at 0.8 μ m (Thales laser, Alpha 100/1000/XS hybrid), and the ions were detected by a Wiley–McLaren time-of-flight mass spectrometer (Toyama, KNTOF-1800) equipped with a Bradbury–Nielsen ion gate,^[30] an offset curved field reflectron,^[16–18] and MCP detectors (Hamamatsu Photonics, F4655-11X). Hexafluorobenzene (Aldrich, 99%) was degassed by repeated freeze-and-thaw cycles before use. Xenon (Japan Air Gases, 99.99%) was used as received. The laser intensity of the linearly polarized pulse at the focus was determined by measuring the saturation intensity of xenon.^[31] SIMION 3D™ version 8.0 (Scientific Instrument Services) was used for ion trajectory simulation.

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Keywords: Femtosecond laser • Ion trajectory simulation • Tunnel ionization

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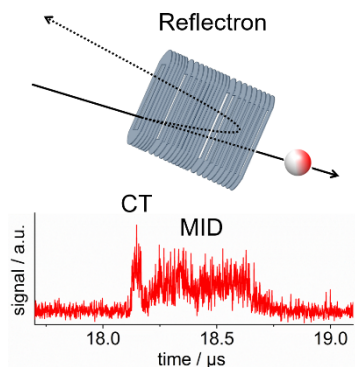
Entry for the Table of Contents (Please choose one layout)

Layout 1:

ARTICLE

Ion detection behind an ion mirror:

Products formed by the charge transfer (CT) or metastable ion dissociation (MID) of multiply charged molecular cations are detected behind the reflectron (ion mirror). They are successfully identified as neutral or cationic species by the disappearance voltage and relative flight time shift without the need of instrument modification.



*Akihiro Kitashoji, Kosei Kitagawa,
Akimasa Fujihara, and Tomoyuki
Yatsunami**

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**Charge Transfer and Metastable Ion
Dissociation of Multiply Charged
Molecular Cations Observed by Using
Reflectron Time-of-Flight Mass
Spectrometry**