

Original Article

# Charge-Dependent Metastable Dissociations of Multiply Charged Decafluorobiphenyl Formed by Femtosecond Laser Pulses

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Femtosecond laser ionization is a unique means to produce multiply charged organic molecules in the gas phase. The charge-dependent chemical reactions of such electron-deficient molecules are interesting from both fundamental and applied scientific perspectives. We have reported the production of quadruply charged perfluoroaromatics; however, they were so stable that we cannot obtain information about their chemical reactions. In general, it might be difficult to realize the conflicting objectives of observing multiply charged molecular ion themselves and their metastable dissociations. In this study, we report the first example showing metastable dissociations of several charge states within the measurable time range of a time-of-flight mass spectrometer. Metastable dissociations were analyzed by selecting a precursor ion with a Bradbury–Nielsen ion gate followed by time-of-flight analysis using a reflectron. We obtained qualitative information that triply and quadruply charged decafluorobiphenyl survived at least in the acceleration region but completely decomposed before entering a reflectron. In contrast, three dissociation channels for singly and one for doubly charged molecular ions were discriminated by a reflectron and determined with the help of ion trajectory simulations.



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## INTRODUCTION

Neutral radicals, cations, and anions are fundamental species in chemistry, biology, and medicine. Further, multiply charged ions have been recognized as important species in those fields. Molecules with multiple positive charges are classified into three groups. Multiply cationized (protonated) molecules were formed by the addition of positive ions (protons) using electrospray ionization and/or matrix-assisted laser desorption/ionization.<sup>1)</sup> Carbopolycations synthesized by removing anionic fragments in the presence of super acids were stable and/or stabilized by ionic species of opposite charges in a liquid medium.<sup>2)</sup> These two species were formed by forming or breaking chemical bonds, *i.e.*, the chemical composition was different from their neutral states. In contrast, multiply charged cation radicals or cations are formed by simultaneously or sequentially stripping electrons from a neutral molecule under extreme conditions such as interstellar space where the molecules are exposed to extreme ultraviolet radiation.<sup>3)</sup> Interactions with strong electric fields

created by intense femtosecond laser pulses or collision with highly charged atomic ions are laboratory-scale preparation methods of extreme conditions to produce such ions.<sup>4)</sup>

We have investigated the production of quadruply charged molecular ions such as triphenylene (C<sub>18</sub>H<sub>12</sub>), 2,3-benzofluorene (C<sub>17</sub>H<sub>12</sub>), hexafluorobenzene (C<sub>6</sub>F<sub>6</sub>), octafluoronaphthalene (C<sub>10</sub>F<sub>8</sub>), and diiodoacetylene (C<sub>2</sub>I<sub>2</sub>) by femtosecond laser ionization followed by their analysis using a time-of-flight mass spectrometer (TOF-MS) with a reflectron, namely refTOF-MS.<sup>5–10)</sup> We further provided the existence of pentuply charged organic molecule.<sup>7)</sup> Since production yield of multiply charged ions became much larger than that obtained by other ionization methods such as electron ionization and vacuum ultraviolet light ionization, investigation of charge-dependent reactions seemed to become a reality. In contrast to singly charged ions, such multiply charged ions show characteristic charge separation reaction (Coulomb explosion) including structure rearrangements before forming fragment ions. Thus, the investigations of their reaction paths depending on their charge and

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multiplicity are worthwhile subjects from fundamental viewpoints and might be useful for the molecular structure determination.<sup>11)</sup> Reconstruction of ion structure based on the investigation of the dissociation channels has been carried out by a variety of methods. One of the most useful means to investigate the dissociation of singly charged ions is tandem spectroscopy.<sup>12)</sup> A refTOF-MS equipped with an ion gate is used for tandem mass spectroscopy as a simple and convenient apparatus.<sup>13–15)</sup> However, the investigation of dissociation channels of multiply charged ions by a refTOF-MS is not straightforward. First, intense femtosecond laser ionization successfully produced multiply charged molecular ions, but somehow it became difficult to study their metastable dissociation taking time longer than few tens of microseconds. Second, we need to consider the problem originating from the working principle of a refTOF-MS: the product ions can pass through a reflectron if their  $m/z$ s were larger than those of a precursor ion.<sup>16)</sup> The dissociation of  $C_6F_6^{z+}$  ( $z=1–4$ ) was explored by selecting a specific charge state as a precursor ion by the Bradbury–Nielsen ion gate (BNG) followed by TOF analysis using the refTOF-MS.<sup>6)</sup> However, the product ion, whose  $m/z$  was smaller than that of a precursor ion, was not observed. It is emphasized that the small amount of product ions whose  $m/z$ s were larger than those of precursor ions were detected behind a reflectron.<sup>16)</sup> The use of a reflectron as a high-energy pass filter does not require the modification of instruments nor precursor ion selection, but losses the resolution and sensitivity of product ion detections. In this study, we investigated decafluorobiphenyl (DFB;  $C_{12}F_{10}$ ) that satisfies two conflicting objectives: production of multiply charged ions and investigation of their metastable dissociations within the measurable time range of the refTOF-MS.

## EXPERIMENTAL

DFB (Aldrich, MO, USA, 99%) purified by sublimation and xenon (Japan Air Gases, 99.99%) were each introduced to an ionization chamber by a leak valve at 296 K. The experimental details have been described elsewhere.<sup>8)</sup> Briefly, multiple ionization of DFB and xenon was carried out using a linearly polarized 40-fs pulse centered at 0.8  $\mu\text{m}$  delivered from a 1-kHz-repetition-rate Ti:Sapphire laser (Alpha 100/1000/XS hybrid; Thales Laser, Paris, France). The pulse width was measured by a second-order single-shot autocorrelator (TAIGA; Thales laser). We also used a linearly polarized 40-fs pulse centered at 1.4  $\mu\text{m}$  delivered from an optical parametric amplifier (TOPAS; Quantronix, UT, USA) pumped by 0.8- $\mu\text{m}$  pulses. The pulse width was measured by a second-order scanning autocorrelator (PulseCheck; APE). The laser beam passed through several quartz optics, such as a beam splitter, a focusing lens, and an ionization chamber window. Quartz plates of the same thickness as these optics were placed in front of the autocorrelators, and group velocity dispersions introduced by these materials were compensated with the acousto-optic programmable dispersive filters (Dazzler; Fastlite, Antibes, France) to have the minimum pulse width. The ions were detected by a Wiley–McLaren TOF-MS equipped with a curved-field reflectron (KNTOF-1800; Toyama, Kanagawa, Japan) as described elsewhere.<sup>16)</sup> The geometry of refTOF-MS and voltage applied to electrodes are shown in Fig. S1. The chamber pressure was monitored 20 cm away from the laser focus point with a cold cathode pressure gauge. The base pressure of the ionization

chamber and the TOF chamber was below  $5 \times 10^{-7}$  Pa. A 500- $\mu\text{m}$ -wide slit was placed on the extraction electrode perpendicular to the laser propagation direction in order to collect the ions that were generated in the most tightly focused point of the laser beam (achieving ion collection from axially symmetric parallel beam geometry). For product ion analysis, a specific precursor ion was selected by the BNG followed by the TOF analysis.<sup>17)</sup> The laser beam was focused into the ionization chamber with a plano-convex quartz lens with a 200-mm focal length. For the cases of 1.4  $\mu\text{m}$  laser pulses, the beam size was expanded by a Galilean-type beam expander before focusing to increase the focused laser intensity. The position of the focusing lens along the laser propagation direction was adjusted so as to maximize the signal intensity of the highest charge state of xenon observed (0.8  $\mu\text{m}$ ,  $\text{Xe}^{5+}$ ; 1.4  $\mu\text{m}$ ,  $\text{Xe}^{3+}$ ). The laser energy was attenuated by the combination of a half-wave plate and plate polarizers before the pulse compressor. A part of the laser beam was reflected by a beam splitter at a small incident angle, and we measured the laser pulse energy using a calibrated Si pin-photodiode in a spectralon-coated integrating sphere (Labsphere, NH, USA). We determined the actual laser intensity of the linearly polarized pulse at the focus by measuring the saturation intensity of xenon ( $1.1 \times 10^{14}$  W  $\text{cm}^{-2}$  for a 45-fs pulse) by the method of Hankin *et al.*,<sup>18)</sup> and the error in the determination of the absolute laser intensity was approximately  $\pm 10\%$ . The experiments of DFB were carried out successively after the measurement of saturation intensity of xenon without changing the experimental conditions between runs. The laser polarization direction was parallel (0.8  $\mu\text{m}$ ) or perpendicular (1.4  $\mu\text{m}$ ) to the ion flight axis. The output signals from the microchannel plate (MCP, F4655-11X; Hamamatsu Photonics, Hamamatsu, Japan) and pin-photodiode were averaged by a digital oscilloscope (Wave Runner 6100, 1 GHz; LeCroy Japan, NY, USA). The ion yield was obtained by integrating over the appropriate peak in the time-of-flight spectrum. SIMION 3D™ version 8.0 (Scientific Instrument Services) was used for ion trajectory simulation. The geometry and voltage applied to electrodes used in simulations were the same as those used in experiments (Fig. S1). The electrostatic potential experienced by a representative ion reflected by a reflectron as a function of flight time is presented in our previous paper.<sup>10)</sup>

## RESULTS AND DISCUSSION

### Ionization of DFB by 0.8- $\mu\text{m}$ femtosecond laser pulses

Figure 1 shows the mass spectra of DFB ionized by 0.8- $\mu\text{m}$  laser pulses with the laser intensity of  $1.8 \times 10^{15}$  W  $\text{cm}^{-2}$ . Since DFB consisted of carbons and fluorines, the elemental composition of fragment ions was easily assigned. The detected ions were atomic ions ( $C^{x+}$ ,  $x=1–3$ ;  $F^{y+}$ ,  $y=1–2$ ), molecular ions ( $\text{DFB}^{z+}$ ,  $z=1, 3$ ;  $C_{12}F_{10}^{z+}$ ,  $z=2, 4$ ), small fragment ions ( $C_2^+$ ,  $C_3^+$ ,  $CF^+$ ,  $CF_2^+$ ,  $CF_2^{2+}$ ), and a series of fragment ions. Actually, we need to denote the molecular ions as  $\text{DFB}^{z+}$  ( $z=1, 3$ ) or  $\text{DFB}^{z+}$  ( $z=2, 4$ ), but we will use  $\text{DFB}^{z+}$  ( $z=1–4$ ) in this study for simplicity. The relative signal intensities of the singly and doubly charged ions are listed in Table S1. The multiply charged atomic ions and small fragment ions were dominantly formed. It is expected that such ions are formed at the most intense central part (the stated intensity of  $1.8 \times 10^{15}$  W  $\text{cm}^{-2}$ ) of the laser beam, where Coulomb explosion of highly charged ions readily occurs.<sup>4)</sup> At the

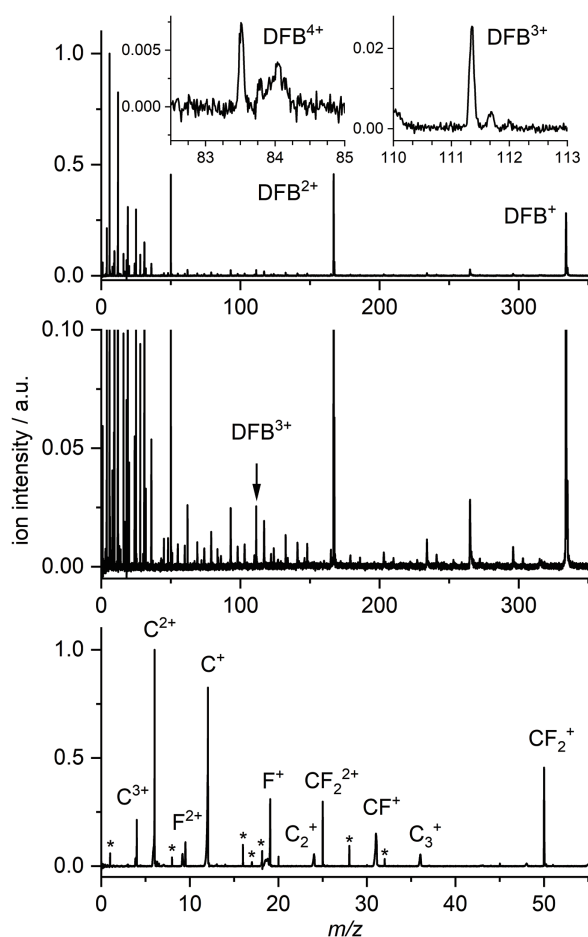


Fig. 1. Mass spectra of DFB measured without using a reflectron. The top and middle panels show the same spectra but with different vertical scales. The bottom panel shows the peaks with  $m/z$  below 55. The insets in the top panel show the magnification of the  $\text{DFB}^{3+}$  and  $\text{DFB}^{4+}$  peaks. The signal intensity of  $\text{C}^{2+}$  was normalized to unity. The laser wavelength was 0.8  $\mu\text{m}$ . The laser intensity was  $1.8 \times 10^{15} \text{ W cm}^{-2}$ . The asterisks indicate the ions originating from contaminated water and air. The pressure in the ion source was  $5.0 \times 10^{-5} \text{ Pa}$ . DFB, decafluorobiphenyl.

same time, molecular ions of low charge state were formed at the wing of the laser beam (in space) as well as the leading and trailing edge of the laser pulse (in time) where the laser intensity is low. Actually, the yields of  $\text{DFB}^+$  and  $\text{DFB}^{2+}$  were saturated at around  $1.7 \times 10^{14} \text{ W cm}^{-2}$  (Fig. S2).  $\text{DFB}^{3+}$  was definitively assigned by the presence of its isotope peak ( $^{13}\text{C}^{12}\text{C}_{11}^{19}\text{F}_{10}^{3+}$ ) at  $m/z$  111.67.  $\text{DFB}^{4+}$  ( $m/z$  83.5) was also present and its isotope peak ( $m/z$  83.75) can be identified over the peak of  $\text{C}_7^+$  ( $m/z$  84). We reported the production of triply and quadruply charged molecular ions of hexafluorobenzene<sup>6)</sup> and octafluoronaphthalene<sup>7)</sup> by 0.8  $\mu\text{m}$  laser pulses. Compared with these molecules, the relative signal intensity of  $\text{DFB}^{3+}$  was very small. We have shown that the laser wavelength is an important factor to form singly charged molecular ions since the photofragmentation of them occurs within the duration of a laser pulse even though they are formed by nonresonant multiphoton ionization and/or tunnel ionization processes.<sup>19,20)</sup> The minimum energy of electronic transition of a singly charged cation radical (HOMO to SOMO) is lower than of a neutral molecule (HOMO to LUMO). Thus, absorption wavelength of a singly charged

cation radical becomes longer than that of neutral molecule. Moreover, intramolecular charge transfer in a biphenyl cation radical shifted its absorption maximum to about 650 nm,<sup>21)</sup> which was longer than that of benzene cation radical (*ca.* 450 nm).<sup>22)</sup> Furthermore, the absorption maximum of DFB shifted to about 900 nm due to the electron-withdrawing substitutions.<sup>23)</sup> The resonant excitation of  $\text{DFB}^+$  would occur with the laser radiation. However, a relatively large amount of  $\text{DFB}^{2+}$ , which was formed by the sequential tunnel ionization of  $\text{DFB}^+$ , was formed.<sup>4)</sup> Thus, the photofragmentation of  $\text{DFB}^+$  might be inefficient compared with the molecules showing wavelength-sensitive fragmentations.<sup>19,20)</sup> We expect the photofragmentation of a triply charged cation radical having odd number of electrons; however, photoionization and photofragmentation processes cannot be separately investigated under our experimental condition. It was, at least, evident that photofragmentation of  $\text{DFB}^{3+}$  within a laser pulse did not efficiently occur because  $\text{DFB}^{3+}$  was detected. The pump and probe experiments including the selection of the ion of target charge state followed by wavelength-tunable photoirradiation are necessary to confirm the expectations.<sup>24)</sup>

Figure 2 compares the magnified mass spectra of the peak around  $\text{DFB}^{z+}$  ( $z=1-4$ ) measured with or without a reflectron. In order to enhance collision-induced dissociation and signal intensity, the pressure in the ion source was increased. Newly appeared peaks detected by using a reflectron were denoted as A to E. The peaks of A to D appeared at non-integer  $m/z$  indicating that they are product ions formed by metastable dissociation of  $\text{DFB}^+$  in the first drift (field-free) region in the refTOF-MS. The peaks of A, B, and D appeared at  $m/z$  where the fragment ions formed in the ion source were not present, whereas those of C and E were overlapped with  $\text{C}_{12}\text{F}_9^+$  ( $m/z$  315) and  $\text{C}_7\text{F}_4^+$  ( $m/z$  160), respectively. The peaks of  $\text{C}_{11}\text{F}_7^+$  and  $\text{C}_{12}\text{F}_8^+$  tail toward longer times (Fig. 2A) since they were formed by the metastable dissociation in the acceleration region. The origin of those energetic ions would be the dissociation of DFB ions, whose charge states are more than five, in the ion source. In contrast, the detection of  $\text{DFB}^{3+}$  and  $\text{DFB}^{4+}$  as sharp peak (magnified in the inset of Fig. 1) indicated that they were sufficiently stable to leave the ion source. However,  $\text{DFB}^{3+}$  and  $\text{DFB}^{4+}$  were missing in the mass spectra taken using a reflectron. The absence of those peaks measured using a reflectron indicated that they were completely decomposed in the first drift region of the refTOF-MS. Since the yields of  $\text{DFB}^{3+}$  and  $\text{DFB}^{4+}$  were too small, newly appeared peak was not identified under the present condition. It should be noted that there might be a concern that  $\text{DFB}^{3+}$  and  $\text{DFB}^{4+}$  could decompose in the electric field of the reflectron. In contrast to DFB, it has been shown that singly to quadruply charged large aromatic hydrocarbons, perfluoroaromatics, and diiodoacetylene did not decay completely in the first drift region in the refTOF-MS.<sup>5-7,9,10)</sup> It is further noted that octafluoronaphthalene pentacation radical produced by 1.4- $\mu\text{m}$  pulses survived in the first drift region even under the high pressure condition ( $1.0 \times 10^{-4} \text{ Pa}$ ) of ion source.

We have reported that perfluoroaromatics were appropriate molecules that form quadruply or pentuply charged ions. These results make us to declare that DFB is a unique model molecule that shows metastable dissociations in four charge states. We could not determine the actual kinetics of such reactions, but we can at least estimate the time ( $t_d$ ) that we

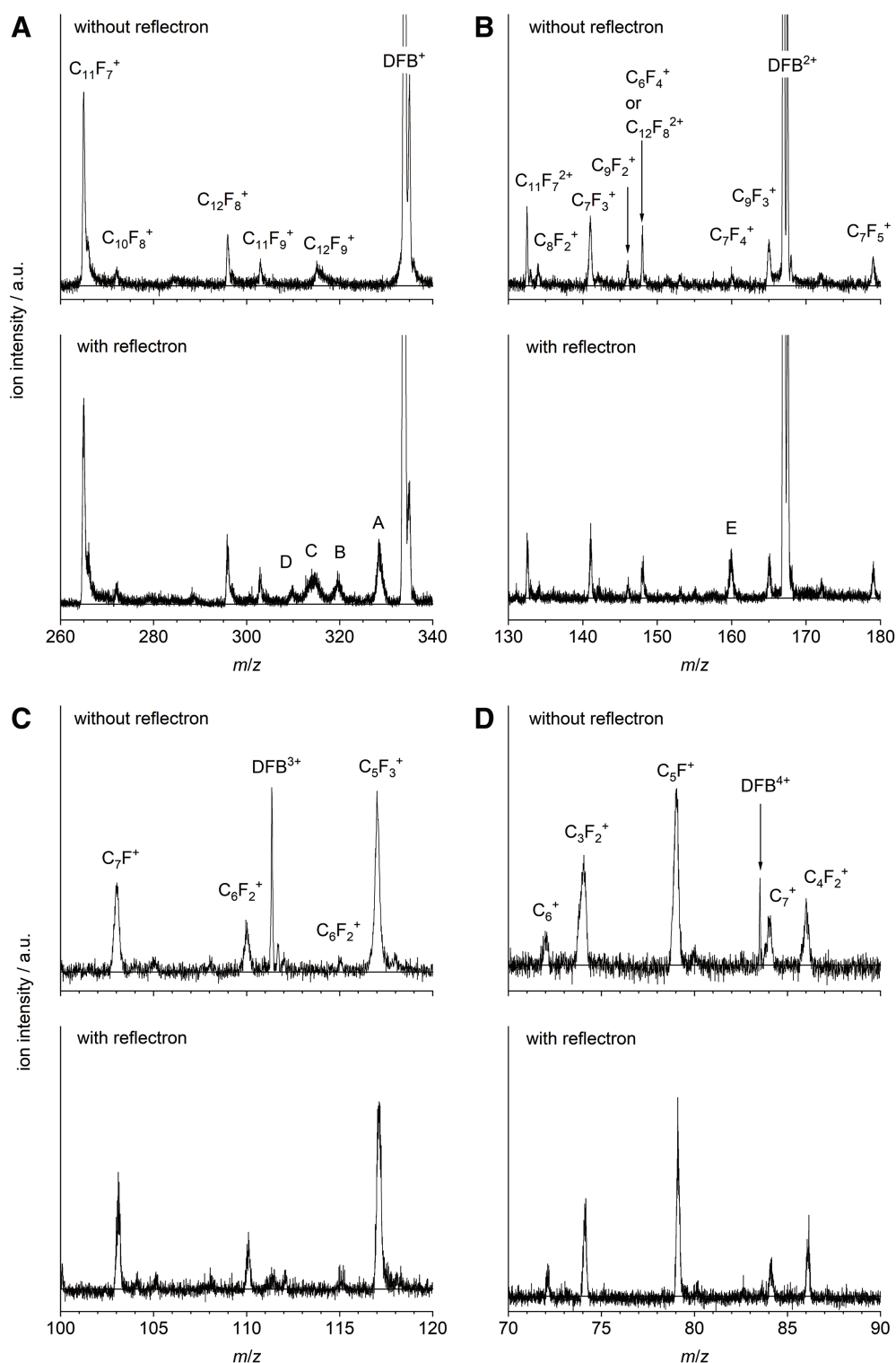


Fig. 2. Magnified mass spectra of the peaks around (A)  $\text{DFB}^+$ , (B)  $\text{DFB}^{2+}$ , (C)  $\text{DFB}^{3+}$ , and (D)  $\text{DFB}^{4+}$  measured without (upper panels) or with a reflectron (lower panels). BNG was not used. The laser wavelength was  $0.8 \mu\text{m}$ . The laser intensity was  $2.8 \times 10^{15} \text{ W cm}^{-2}$  (without a reflectron) and  $1.3 \times 10^{15} \text{ W cm}^{-2}$  (with a reflectron). Pressure in the ion source was  $2.0 \times 10^{-4} \text{ Pa}$ . (A–E) indicate the candidates of product ions. BNG, Bradbury-Nielsen ion gate; DFB, decafluorobiphenyl.

can detect ions based on the flight time in the acceleration region ( $t_1$ ) and the flight time in the first drift region ( $t_2$ ). Although  $t_d$  is not a precise quantitative measure like lifetime, it would be a qualitative index indicating that the ion count exceeds the detection limit under our experimental condition. Supposing that the ion was detected without using a reflectron, its  $t_d$  was greater than  $t_1$  ( $\text{DFB}^{3+}$ ,  $0.6 \mu\text{s}$ ;  $\text{DFB}^{4+}$ ,  $0.5 \mu\text{s}$ ). If the ion was not detected after reflected by a reflectron, its  $t_d$  was

less than the sum of  $t_1$  and  $t_2$  ( $\text{DFB}^{3+}$ ,  $16 \mu\text{s}$ ;  $\text{DFB}^{4+}$ ,  $14 \mu\text{s}$ ). In contrast,  $t_d$ s of ions that were detected using a reflectron were greater than the sum of  $t_1$  and  $t_2$  ( $\text{DFB}^+$ ,  $27 \mu\text{s}$ ;  $\text{DFB}^{2+}$ ,  $19 \mu\text{s}$ ).

### Selection of a precursor ion by using a BNG

$\text{DFB}^+$  and  $\text{DFB}^{2+}$  were each selected as a precursor ion by the BNG for further analysis. Figure 3 shows the magnified TOF spectra measured with or without using the BNG. The



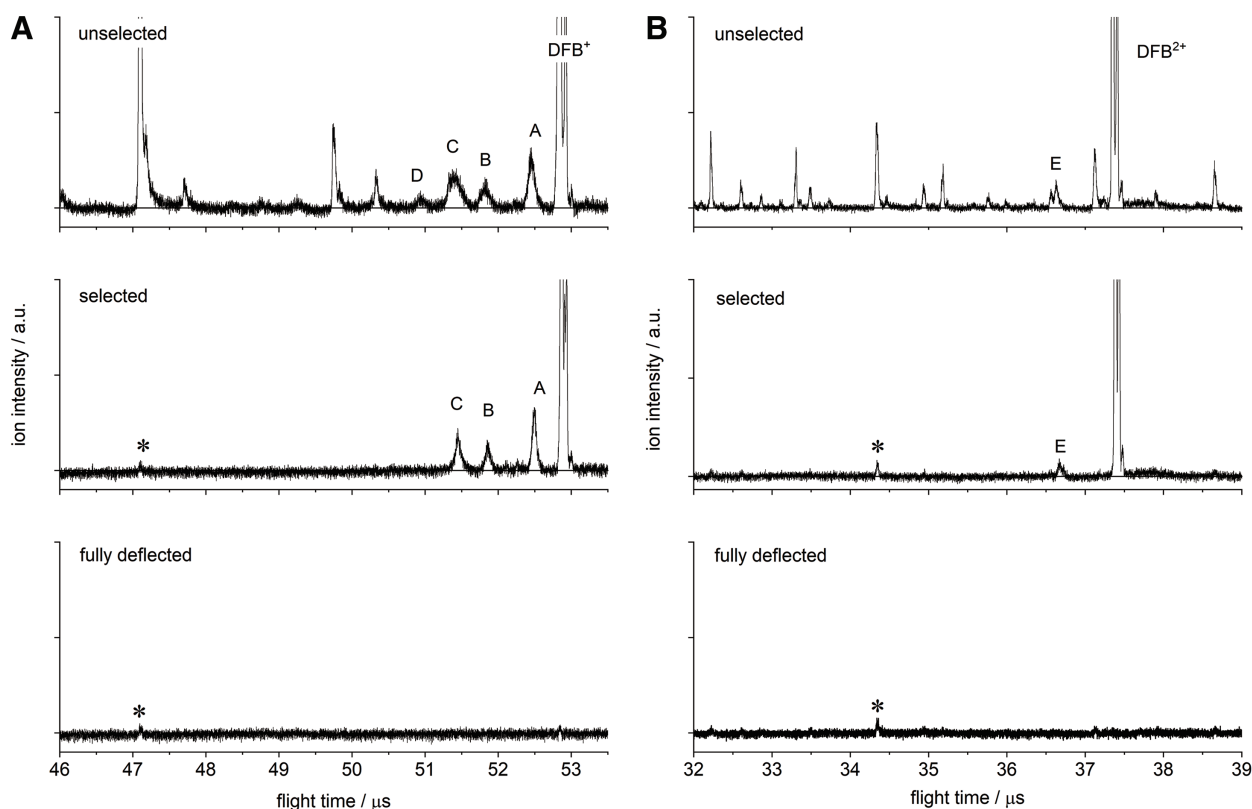


Fig. 3. Magnified TOF spectra of the peaks around (A) DFB<sup>+</sup> and (B) DFB<sup>2+</sup> measured without selecting precursor ion (top panels), with selecting precursor ion (middle panels), and by deflecting all ions (bottom panels). The width of high voltage applied to BNG was adjusted to selectively pass DFB<sup>+</sup> (230 ns) and DFB<sup>2+</sup> (130 ns), respectively. A high voltage was continuously applied to the BNG to deflect ions appearing in the observed time region. The asterisks indicate the peak originating from the electrical noise. A reflectron was used. The laser wavelength was 0.8 μm. Laser intensity was  $2.8 \times 10^{15}$  W cm<sup>-2</sup>. The pressure in the ion source was  $2.0 \times 10^{-4}$  Pa. BNG, Bradbury–Nielsen ion gate; DFB, decafluorobiphenyl; TOF, time of flight.

actual ion selection ability, *i.e.*, the gate function, of BNG was  $36.5 \pm 0.5$  ns (fwhm) in width,<sup>17)</sup> which was sufficient to select a monoisotopic DFB<sup>+</sup> and DFB<sup>2+</sup>. The width of the gate and the timing with respect to a laser pulse were optimized to maximize the signal intensity of precursor ions. After the selection of DFB<sup>+</sup>, the peaks A to C were observed while that of D was missing. Therefore, the peak D would presumably be a secondary product of DFB<sup>+</sup>. The peaks C and E became sharpened after the precursor ion selection because the other fragment ions formed in the ion source were removed. It is noted that peaks indicated by asterisks were observed even after deflecting all ions by continuously applying high voltage to the BNG. They were not the peaks of product ions but the electronic noises caused by high-voltage power supply. Since the fragment ions formed in the ion source were well separated, we can say that three and one species were formed from DFB<sup>+</sup> and DFB<sup>2+</sup>, respectively, in the first drift region.

### Product ion determination using ion trajectory simulations

The  $m/z$ s of the product ions formed from a specific precursor ion were estimated using an ion trajectory simulation based on the optimized ion optics configurations. The difference of the flight times ( $\Delta$ TOF) between calculated ones using an ion trajectory simulation and experimentally obtained ones using a reflectron for DFB<sup>+</sup> was 0.11 μs corresponding to 0.21% with respect to the TOF measured experimentally. This error might be attributed to the limited

precision of the ion optics configurations in the simulation. Roughly speaking,  $\Delta$ TOF of 0.1 μs corresponded to the  $m/z$  range of 5. The accuracy of simulation thought not to be enough for hydrocarbons but could be allowed for fluorocarbons. The widths of the peaks (fwhm) of A, B, C, and E shown in the middle panels of Fig. 3 were 75, 93, 107, and 82 ns, respectively, which were comparable to  $\Delta$ TOF. We thus simulate flight time of product ions under this condition. In the cases of product ion analysis, we need to consider the problem originating from the working principle of a reTOF-MS. The  $m/z$  range of product ions formed from a multiply charged precursor ion was limited because the product ions can pass through a reflectron if their  $m/z$ s were larger than that of a precursor ion.<sup>16)</sup> Based on the voltages applied to each ion optics and their configurations, the range of the  $m/z$  of the product ions of DFB<sup>2+</sup> ( $m/z$  167) that can be reflected by a reflection was between 1 and 236. Further, the product ions that collide to the effective area of an MCP were also limited under our fixed experimental conditions. The detectable ranges of  $m/z$  of the product ions were simulated to be 101–333 for DFB<sup>+</sup> and 51–196 for DFB<sup>2+</sup>. It is noted that the above simulated range of  $m/z$  might include errors because the effective area of MCP was not accurately simulated.

Although the elemental composition of fragment ions was easily assigned because DFB consisted of carbons and fluorines, the possible combination of C<sub>*m*</sub>F<sub>*n*</sub> ( $m=0-12$ ,  $n=0-10$ ,  $m+n \neq 0$ ) was 142. Thus, the possible number of product ions of DFB<sup>+</sup> was 141. Supposing that doubly charged product

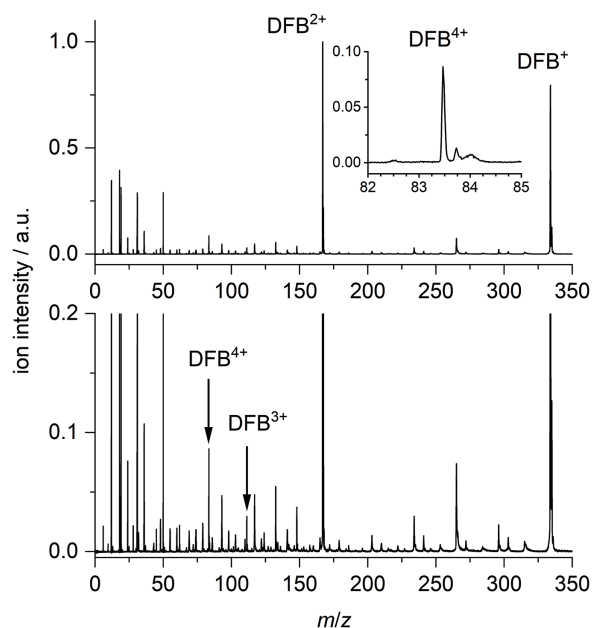


Fig. 4. Mass spectra of DFB measured without using a reflectron. The upper and lower panels show the same spectra but with different vertical scales. The inset in the upper panel shows the magnification of the  $\text{DFB}^{4+}$  peaks. The signal intensity of  $\text{DFB}^{2+}$  was normalized to unity. The laser wavelength was 1.4  $\mu\text{m}$ . The laser intensity was  $4.2 \times 10^{14} \text{ W cm}^{-2}$ . The pressure in the ion source was  $5.0 \times 10^{-5} \text{ Pa}$ . DFB, decafluorobiphenyl.

Table 1. Possible metastable dissociation channels of  $\text{DFB}^+$  and  $\text{DFB}^{2+}$ .

Product ion	Candidates			Detectability <sup>a</sup>	TOF ( $\mu\text{s}$ )		$\Delta\text{TOF}$ ( $\mu\text{s}^b$ )
	Formula	$m/z$	Counter species		Experiment	Simulation	
A	$\text{C}_{10}\text{F}_{10}^+$	310	$\text{C}_2$	N (N)	52.494	52.3539	0.140
	$\text{C}_{12}\text{F}_9^+$	315	F	Y (Y)		52.4613	0.032
	$\text{C}_{11}\text{F}_{10}^+$	322	C	N (N)		52.6095	-0.115
B	$\text{C}_{11}\text{F}_8^+$	284	$\text{CF}_2$	Y (Y)	51.862	51.7874	0.074
	$\text{C}_8\text{F}_{10}^+$	286	$\text{C}_4$	N (N)		51.8316	0.030
	$\text{C}_{10}\text{F}_9^+$	291	$\text{C}_2\text{F}$	N (N)		51.9416	-0.079
C	$\text{C}_{11}\text{F}_7^+$	265	$\text{CF}_3$	Y (Y)	51.448	51.3630	0.085
	$\text{C}_8\text{F}_9^+$	267	$\text{C}_4\text{F}$	N (Y)		51.4081	0.039
	$\text{C}_{10}\text{F}_8^+$	272	$\text{C}_2\text{F}_2$	Y (Y)		51.5204	-0.072
	$\text{C}_7\text{F}_{10}^+$	274	$\text{C}_5$	N (N)		51.5652	-0.117
E	$\text{C}_7\text{F}_3^+$	141	$\text{C}_5\text{F}_7^+$	Y (Y)	36.672	36.6093	0.062
	$\text{C}_{11}\text{F}_8^{2+}$	142	$\text{CF}_2$	Y (Y)		36.6476	0.024
	$\text{C}_8\text{F}_{10}^{2+}$	143	$\text{C}_4$	N (N)		36.6611	0.010
	$\text{C}_{12}^+$	144	$\text{F}_{10}^+$	N (N)		36.6923	-0.020
	$\text{CF}_7^+$	145	$\text{C}_{11}\text{F}_3^+$	N (N)		36.7234	-0.051
	$\text{C}_{10}\text{F}_9^{2+}$	145.5	$\text{C}_2\text{F}$	N (N)		36.7389	-0.066
	$\text{C}_9\text{F}_2^+$	146	$\text{C}_3\text{F}_8^+$	Y (Y)		36.7544	-0.082

<sup>a</sup>Ions observed (Y) or not observed (N) in this experiment without using a reflectron or by electron ionization (see Table S1). The results for electron ionization experiment are shown in parentheses.

<sup>b</sup>Calculated by subtracting experimentally measured TOF from simulated TOF. DFB, decafluorobiphenyl; TOF, time of flight.

ions form, the number of possible  $m/z$  of the product ions of  $\text{DFB}^{2+}$  was 242 as listed in Table S1. However, this list contained unrealistic combinations, for example,  $\text{F}_5^+$  and  $\text{F}_{10}^{2+}$ . We need to consider the ions that can be stable enough during the first drift region to be detected. To further investigate the candidates of product ions, we ionized DFB by a 1.4- $\mu\text{m}$  laser pulse as shown in Fig. 4. It is noted that the isotope peak ( $^{13}\text{C}^{12}\text{C}_{11}^{19}\text{F}_{10}^{4+}$ ) of  $\text{DFB}^{4+}$  was clearly observed at  $m/z$  83.75. The correlation between ion yield and laser intensity is shown in Fig. S3. Table S1 shows the relative signal intensity of ions formed by 0.8 and 1.4  $\mu\text{m}$  laser pulses. For reference, data taken by electron ionization are also listed. The number of ion peaks formed by 0.8 and 1.4  $\mu\text{m}$  laser pulses with ion signal

intensity more than 0.5% of that of base peak (0.8  $\mu\text{m}$ ,  $\text{C}^+$ ; 1.4  $\mu\text{m}$ ,  $\text{DFB}^{2+}$ ) was 36 and 49, respectively. Consequently, the number of possible fragment ions formed by 0.8 and/or 1.4  $\mu\text{m}$  femtosecond laser pulses was 51 by subtracting duplicates. It is noted that 8 fragment ions were solely assigned to be doubly charged species. Finally, the limitation of the detectable range of  $m/z$  reduced the number of  $m/z$  for the possible product ions to be 23 ( $\text{DFB}^+$ ) and 29 ( $\text{DFB}^{2+}$ ). For reference purpose, we checked the relatively small fragment ions, whose intensity was less than 0.5% of that of base peak in Table S1.

Supposing that two-body fragmentation occurs in  $\text{DFB}^+$  and  $\text{DFB}^{2+}$ , we can list the candidates of the product ions A, B, C, and E in Table 1. We selected possible species by limiting

$\Delta$ TOF to be smaller than 0.15  $\mu$ s for product ions A, B, and C, and 0.10  $\mu$ s for product ion E. The list includes the detectability, *i.e.*, whether the candidates were observed by our TOF-MS or not. Ions that were not observed by our TOF-MS or electron ionization (EI) were excluded from the candidates. Therefore, the most probable product ions were determined for A to be  $C_{12}F_9^+$  and for B to be  $C_{11}F_8^+$ . In contrast, we can raise two candidates ( $C_{11}F_7^+$ ,  $C_{10}F_8^+$ ) for the product ion C and three candidates ( $C_7F_3^+$ ,  $C_{11}F_8^{2+}$ ,  $C_9F_2^+$ ) for the product ion E. Supposing that the relative intensity of these ions (Table S1) reflected their stability, we further selected  $C_{11}F_7^+$  for C and  $C_7F_3^+$  for E.  $C_5F_7^+$  ( $m/z$  193), which was considered to be the counter ion of  $C_7F_3^+$  ( $m/z$  141) in the charge separation of  $DFB^{2+}$ , did not appear at the simulated TOF in Fig. 3. The absence of  $C_5F_7^+$  peak was probably not because it was out of the detectable range but because it dissociated into small fragments. Certainly, this ion was not observed by our TOF-MS without using a reflectron nor electron ionization.

## CONCLUSIONS

The highest charge state of DFB produced by 0.8- and 1.4- $\mu$ m intense femtosecond laser pulses in the gas phase was  $DFB^{4+}$ . The analysis of product ions emerged from  $DFB^{3+}$  and  $DFB^{4+}$ , which were completely decomposed in the first drift region in the refTOF-MS, was not possible because their yields were too small. In contrast, we successfully observed the product ions of  $DFB^+$  and  $DFB^{2+}$ . We suggested F,  $CF_2$ , and  $CF_3$  liberations from  $DFB^+$  and charge-separation reaction of  $DFB^{2+}$  based on the flight time simulations and detectability of fragment ions. Unlike the perfluoroaromatics we have considered so far, it is emphasized that DFB shows characteristic charge-dependent metastable reactions in the four charged states. However, it should be emphasized that we might miss the product ions of  $DFB^{2+}$ , which can pass through a reflectron. Therefore, further improvement of the accuracy of simulation and the complementary detection of the ions that were reflected and passed through a reflectron would be necessary to achieve full product ion analysis. Our approach has been making use of conventional instruments without modification to achieve full product ion analysis of multiply charged ion, but the alternative product ion detection method is necessary to investigate the kinetics of metastable dissociations as well as more complex and highly charged molecules. Ion storage rings<sup>25)</sup> as well as multi-turn TOF-MS<sup>26,27)</sup> maintained under a high vacuum condition can hold multiply charged ions for a long time and presumably investigate the kinetics of metastable dissociations.

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