

Definitive production of intact organic pentacation radical: Octafluoronaphthalene ionized in intense femtosecond laser fields

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概要	芳香族フッ素化合物にフェムト秒レーザーを照射することで、有機化合物では初となる 5 価陽イオンを生成することに成功しました。 フェムト秒レーザーを用いることで、有機化合物陽イオンの価数の最大値を 49 年ぶりに更新しました。 ‘有機化合物初の 5 価陽イオン・芳香族最小の 4 価陽イオンの生成～フェムト秒レーザーの活用によって～’ 大阪市立大学. https://www.osaka-cu.ac.jp/ja/news/2019/191001-2 . (参照 2019-10-02)
Relation	芳香族化合物では最も小さい 4 価陽イオンを生成することに成功 https://dlistv03.media.osaka-cu.ac.jp/il/meta_pub/G0000438repository_13480715-48-12-1472

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**Definitive production of intact organic pentacation radical:
Octafluoronaphthalene ionized in intense femtosecond laser fields**

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ABSTRACT

We demonstrate the production of long-lived octafluoronaphthalene pentacation radical in gas phase by tunneling ionization using 1.4 μm femtosecond laser pulses. Multiply charged molecular cations are definitively identified by their m/z , isotopic structure, and peak shape using time-of-flight mass spectrometry. The tetracation yield relative to the trication radical yield is 0.33 that is the highest value obtained to date. The yield of pentacation radical relative to tetracation is 0.025. Our results show that the use of perfluoro-aromatics is the promising way to approach intact highly charge states.

Key words

Femtosecond laser, Mass spectrometry, Time-of-flight, Tunnel ionization

1. Introduction

The production of multiply charged ion has become popular by the invention of electro spray ionization [1, 2]. The attachment of several protons to a molecule produces multiply charged species that is stable enough to be analyzed by mass spectroscopy under atmospheric conditions. The removal of several electrons from a molecule can also create multiply charged species. We call this species that keep their original chemical composition as multiply charged molecular cations (MMCs). In contrast to multiply protonated molecules, MMCs are unstable in nature due to the lack of bonding electrons and strong Coulomb repulsions within the molecules [3, 4]. Nevertheless, MMCs are interesting species because several attractive properties such as high electron affinity, high potential energy, high density of electronic states with various spin multiplicities and charge-dependent chemistry are expected. The fundamentals and some applications of organic dication and trication radical have been reviewed in detail [5-9]. In contrast, little is known about the MMCs with the charge number equal to and/or higher than four. Only a few tetracations of inorganic molecules [10, 11] and large aromatic hydrocarbons [12, 13] have been reported. Significant improvements of tetracation yields, which is indispensable to investigate the properties as well as reactions, become possible by

femtosecond laser ionization [14] as well as by the collision with high energy projectiles [15]. For example, Bhardwaj et al. reported C_{60}^{12+} that is the highest charge number obtained to date for inorganic molecules [16]. It is emphasized that the production of intact MMCs by femtosecond laser pulses is dependent on the wavelength [17, 18], polarization [19], and pulse duration [20]. Moreover, the use of halogenated molecules instead of hydrocarbons is advantageous against the dissociation since the ejection of protons by Coulomb explosion does not occur. We present the halogen substitution effects on the production of $ICCI^{4+}$ that is the smallest organic tetracation ever reported to date [21, 22]. The stability of $ICCI^{4+}$ is explained in terms of charge localization on the terminal iodine atoms, which leads to minimum Coulomb repulsion between adjacent atoms [23]. Recently, we successfully produced $C_6F_6^{4+}$ that is the smallest aromatic tetracation [24].

Some reports have indicated the presence of organic pentacation radical using mass spectrometry [15, 25]. In this study, we demonstrate the production of pentacation radical of octafluoronaphthalene in intense femtosecond laser fields based on the following evidences: 1) main peak appeared at appropriate m/z , 2) isotope peak appeared at appropriate m/z , 3) appropriate isotopic structure (peak area ratio) expected by chemical composition and isotope abundance, and 4) peak shape.

2. Experimental

Octafluoronaphthalene (Aldrich, 96%) and xenon (Japan Air Gases, 99.99%) were used as received. The experimental details have been described elsewhere [14, 22]. The pressure of C₁₀F₈ was 5×10⁻⁵ Pa unless otherwise stated. Briefly, the multiple ionization of octafluoronaphthalene and xenon was carried out with a 30-fs pulse centered at 0.8 μm (Thales laser, Alpha 100/1000/XS hybrid). The pulse width was measured by a second-order single-shot autocorrelator (Thales laser, TAIGA). We also used a 40-fs pulse centered at 1.4 μm delivered from optical parametric amplifier (Quantronix, TOPAS) pumped by 0.8 μm pulse. The pulse width was measured by a second-order scanning autocorrelator (APE, PulseCheck). The laser beam was focused into the ionization chamber with a planoconvex quartz lens of 200 mm focusing length. The ions were detected by a linear mode of Wiley–McLaren type time-of-flight mass spectrometer (TOF-MS, Toyama, KNTOF-1800) equipped with a MCP detector (Hamamatsu Photonics, F4655-11X). For the determination of the lower limit of the lifetime of MMC, TOF-MS with a curved-field reflectron was used to distinguish a precursor MMC from those of fragment ions formed by the metastable decay in the drift region [23]. A slit of 500 μm width was located on the extraction plate perpendicular to the laser propagation direction

in order to collect the ion that was generated in the most tightly focused point of the laser beam (achieving ion collection from axially symmetric parallel beam geometry). The actual laser intensity at the focus was determined by measuring the saturation intensity of xenon by the method of Hankin et al. [26], and the error in the determination of absolute laser intensity was about $\pm 10\%$. The m/z scale was calibrated by using xenon ion peaks (Xe^{z+} , $z = 1-6$). The molecular ion yield was obtained by integrating over the appropriate peak ($^{12}\text{C}_{10}\text{F}_8^{z+}$, $z = 1-5$) in the TOF spectrum. The error in the evaluation of the ion yield was approx. $\pm 5\%$.

3. Results and discussion

Fig.1 shows the TOF mass spectra of C_{10}F_8 ionized by 0.8 μm and 1.4 μm pulses. As expected by analogy to previously explored molecules [14], fragmentations were suppressed by using 1.4 μm pulses. All peaks were successfully assigned to $\text{C}_m\text{F}_n^{z+}$ ($m = 0-10$, $n = 0-8$, $m = n \neq 0$, $z = 1-4$) based on their m/z . It is noted that the maximum charge number of naphthalene (C_{10}H_8) was three by using 1.4 μm femtosecond laser pulses [27]. Here, we focus our attention on the production of intact MMCs ($\text{C}_{10}\text{F}_8^{z+}$). Cation radical, dication, trication radical, and tetracation were clearly observed in both 0.8 and 1.4 μm ionization cases. However, there might be some doubt that, for example, the peak at m/z 68 consists of superimposed peaks from $^{12}\text{C}_{10}\text{F}_8^{4+}$ and $^{12}\text{C}_5\text{F}_4^{2+}$. Similarly, $^{12}\text{C}_5\text{F}_4^+$ and

$^{12}\text{C}_{10}\text{F}_8^{2+}$ will appear at the same m/z (136). These concerns are important when we assign the ions with even charge numbers. The key to distinguish them is the presence of isotope peak(s). Supposing that $\text{C}_5\text{F}_4^{2+}$ and C_5F_4^+ are formed, the corresponding isotope peaks such as $^{13}\text{C}^{12}\text{C}_4\text{F}_4^{2+}$ and $^{13}\text{C}^{12}\text{C}_4\text{F}_4^+$ should appear at m/z 68.5 and 137, respectively. The presence of a peak at m/z 68.25 and the absence of a peak at m/z 68.5 indicates that a peak appeared at m/z 68 is not $^{12}\text{C}_5\text{F}_4^{2+}$ but $^{12}\text{C}_{10}\text{F}_8^{4+}$. Similarly, a peak appeared at m/z 136 is assigned to be $^{12}\text{C}_{10}\text{F}_8^{2+}$.

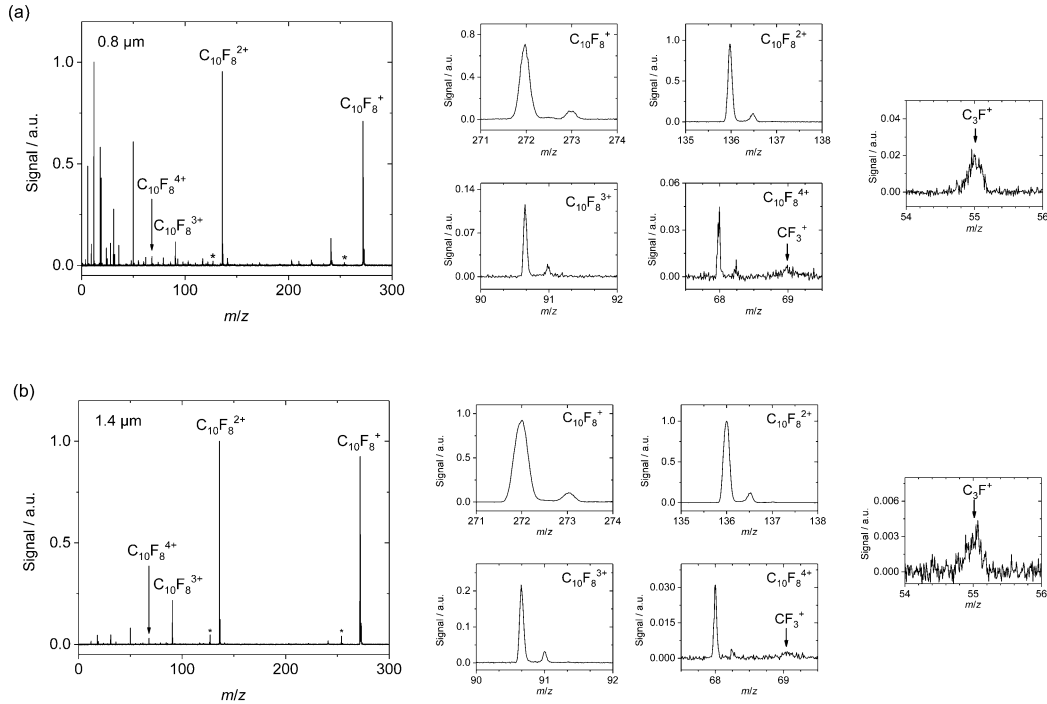


Fig. 1. Time-of-flight mass spectra of C_{10}F_8 ionized by (a) $0.8 \mu\text{m}$ pulse at $4.5 \times 10^{14} \text{ W cm}^{-2}$ and by (b) $1.4 \mu\text{m}$ pulse at $3.7 \times 10^{14} \text{ W cm}^{-2}$. The right panels show the magnification of the same spectrum. The asterisks indicate the ions originating from contaminated

C₁₀F₇H.

In contrast to molecular ions with even charge number, those with odd charge number have unique m/z among 399 possible combinations of m/z for $C_mF_n^{z+}$ ($m = 0-10$, $n = 0-8$, $m = n \neq 0$, $z = 1-5$). Singly and triply charged C₁₀F₈ were clearly visible as single peaks at m/z 272 and 90.66, respectively. Pentacation radical is expected to appear at m/z 54.4, if it exists. We cannot detect this expected peak in the case of 0.8 μm experiments, whereas we could see a small hump by 1.4 μm pulse ionization. Thus, we performed the experiment with better resolution and under high pressure condition (4.4×10^{-4} Pa). By using 1.4- μm pulses, we successfully detected the distinct peaks in the m/z 54–55 region. Three peaks in Fig. 2 were tentatively assigned to $^{12}\text{C}_{10}\text{F}_8^{5+}$, $^{13}\text{C}^{12}\text{C}_9\text{F}_8^{5+}$, and C_3F^+ , respectively, based on their m/z s. The broadening and distortion of the C_3F^+ peak is attributed to the spatial distribution of C_3F^+ . Due to the spatial distribution of laser intensity, $\text{C}_{10}\text{F}_8^{5+}$ is formed at the most intense part of the laser pulse, whereas fragment ion such as C_3F^+ originating in the dissociation of low charge states is formed at the wing of the laser beam where the laser intensity is low. Therefore, the spatial distribution of C_3F^+ is anisotropic and much broader than that of $\text{C}_{10}\text{F}_8^{5+}$ [28]. We fitted these three peaks by five Gaussian functions to resolve the overlap between $^{13}\text{C}^{12}\text{C}_9\text{F}_8^{5+}$ and C_3F^+ peaks. We obtained the peak area of $^{13}\text{C}^{12}\text{C}_9\text{F}_8^{5+}$ relative to that of $^{12}\text{C}_{10}\text{F}_8^{5+}$ to be 0.12,

which is close to the expected value (0.11) calculated by the isotope abundance and chemical composition within the experimental error. We conclude that the peak appeared at m/z 54.4 is originated in $^{12}\text{C}_{10}\text{F}_8^{5+}$ based on the m/z s and peak area ratio. The detection of pentacation radical indicated that it was sufficiently stable to leave the ion source intact; thus, the lifetime of pentacation radical was longer than their acceleration times (>0.56 μs) in the mass spectrometer. Furthermore, we detected pentacation radical by using an offset curved-field reflectron, which can distinguish metastable ion decay in the drift region in the mass spectrometer. It is surprising that pentacation radical does not decay completely at least for 11 μs , which is the flight time of pentacation radical from the ion source to the entrance of the reflectron, even under the high pressure condition (1.0×10^{-4} Pa) of ion source.

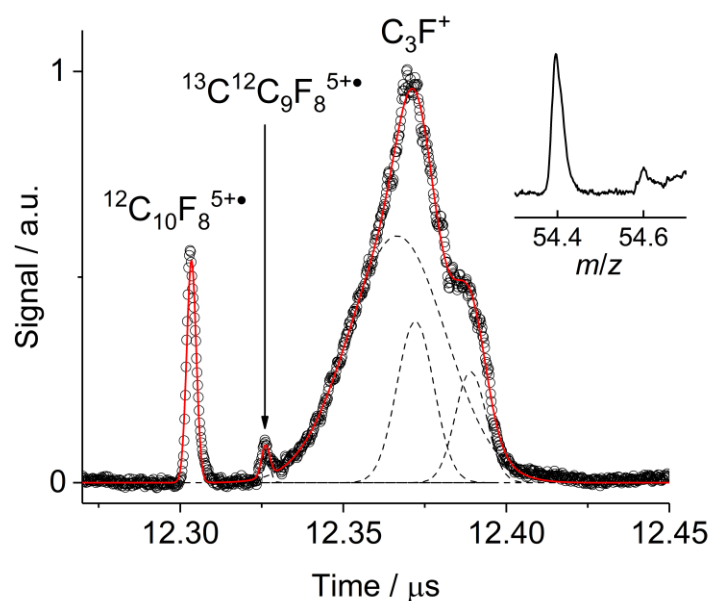


Fig.2. Time-of-flight spectrum of C_{10}F_8 ionized by 1.4 μm pulse at $3.6 \times 10^{14} \text{ W cm}^{-2}$. The

experimental data (open circles) are fitted by five Gaussian functions (broken lines). Solid line is the sum of five Gaussian functions. Inset shows mass spectrum (m/z 54.2–54.8 region).

We note that another important feature of multiply charged species appeared in a TOF spectrum is the width of the peak because the peak width reflects the spatial distribution of ion in the ion source as mentioned for C_3F^+ . The highest charged ion will appear as the narrowest peak since it is formed at the most intense part of the laser beam. The resolutions of the $^{12}C_{10}F_8^{z+}$ peaks ($m/\Delta m$, fwhm) obtained by 0.8 μm pulse (Fig. 1a) were 1.11×10^3 ($z = 1$), 1.31×10^3 ($z = 2$), 1.64×10^3 ($z = 3$), and 1.63×10^3 ($z = 4$), respectively. Those obtained by 1.4 μm pulse (Fig. 1b) were 802 ($z = 1$), 918 ($z = 2$), 1.33×10^3 ($z = 3$), and 1.49×10^3 ($z = 4$), respectively. Relatively better resolution obtained by 0.8- μm pulse ionization is attributed to the nearly Gaussian beam profile of the 0.8- μm laser pulses compared with that of the 1.4- μm laser pulses. The resolution of the $^{12}C_{10}F_8^{5+}$ peak (Fig. 2) was 1.80×10^3 , which is nearly the upper limit (1.9×10^3 obtained for $^{132}Xe^{6+}$) under the present experimental condition [29].

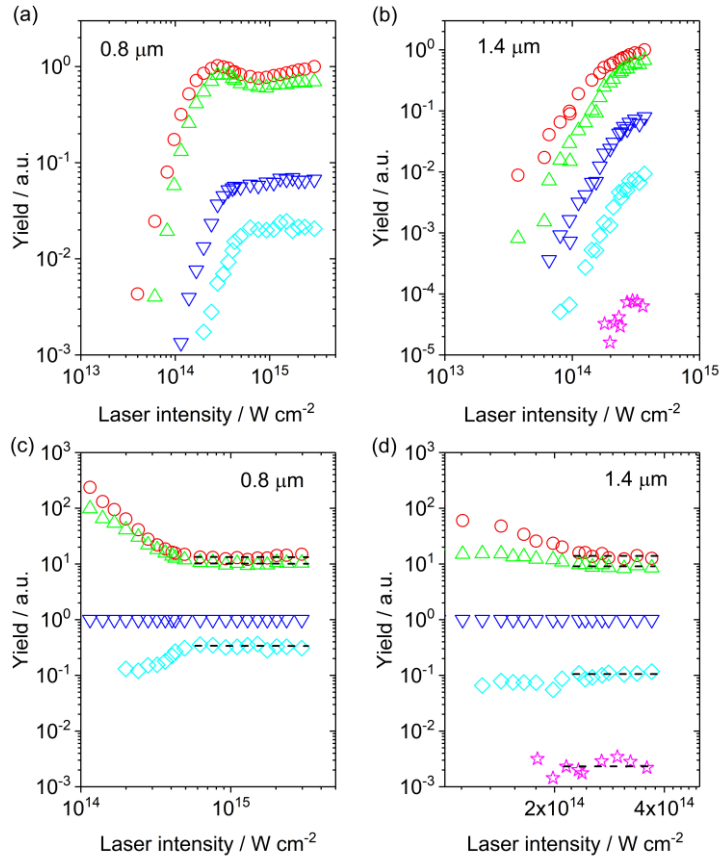


Fig.3. (a, b) Ion yields and (c, d) ion yields relative to that of $C_{10}F_8^{3+}$ as a function of laser intensity. $C_{10}F_8$ was ionized by (a, c) 0.8 μm and (b, d) 1.4 μm pulse: circles ($C_{10}F_8^+$), triangles ($C_{10}F_8^{2+}$), inverted triangles ($C_{10}F_8^{3+}$), diamonds ($C_{10}F_8^{4+}$), stars ($C_{10}F_8^{5+}$). Broken lines indicate the asymptotic (averaged) values.

Fig. 3 (a,b) shows MMC yields as a function of laser intensity. The ion yields increased very steeply as laser intensity increased until it reached the saturation region. After reaching that region, the ion yield stayed constant. The step-like behavior observed for $C_{10}F_8^+$ and $C_{10}F_8^{2+}$ in the case of 0.8 μm ionization was attributed not to physical reasons but to experimental issues explained by the anisotropic spatial distribution of

these ions along the ion flight axis [28]. Fig.3 (c,d) shows the ion yields relative to that of $C_{10}F_8^{3+}$. Above the saturation region, the relative ion yield became nearly constant. The asymptotic (averaged) values obtained by 0.8 μm pulse (Fig. 3c) were 13.3 ($z = 1$), 10.2 ($z = 2$), and 0.33 ($z = 4$), respectively. Those obtained by 1.4 μm pulse (Fig. 3d) were 14.1 ($z = 1$), 9.13 ($z = 2$), 0.10 ($z = 4$), and 2.5×10^{-3} ($z = 5$), respectively. In 2010, we showed the dramatic increase of the aromatic hydrocarbon tetracation yield by femtosecond laser pulses (1.4 μm , 130 fs) compared with that by electron ionization. The yields of tetracation relative to that of trication radical were 0.20 (triphenylene, $^{12}C_{18}H_{12}$) and 0.08 (2,3-benzofluorene, $^{12}C_{17}H_{12}$) [14]. We also showed the abundant production of multiply charged iodine substituted acetylenes. Their tetracation yields relative to trication radical obtained by femtosecond laser pulses (0.8 μm , 40 fs) were 0.12 (diiodoacetylene, $^{12}C_2I_2$) and 0.21 (diiododiacetylene, $^{12}C_4I_2$) [23]. The highest value (0.33) obtained in this study might be attributed to the absence of C-H bond as well as the use of short duration laser pulses. The efficient productions of multiply charged cations are attributed to the adiabatic tunnel ionization processes in femtosecond laser fields [27]. In addition, the resonance-induced fragmentation of cations can be suppressed when a longer wavelength laser pulse is used for ionization [27]. Here, we compare the saturation intensity, I_{sat} , which is the index of ionization rate [30]. Saturation intensity is defined as

the point at which the ion yield (linear scale), extrapolated from the high-intensity linear portion of the curve, intersects the intensity axis (logarithmic scale). I_{sat} s of $\text{C}_{10}\text{F}_8^{z+}$ produced by 1.4 μm pulses were 9.1×10^{13} ($z = 1$), 1.3×10^{14} ($z = 2$), 1.5×10^{14} ($z = 3$), and 1.7×10^{14} W cm^{-2} ($z = 4$), respectively. I_{sat} of pentacation radical was not obtained due to the insufficient data plots to be extrapolated. Since the multiply charged cations were produced in a narrow range of laser intensity, which is not expected for multiphoton process, we conclude that multiply charged cations are produced by the sequential tunnel ionization as in the case of naphthalene [27]. In order to know why pentacation radical is stable at least 11 μs , we need to carry out theoretical calculations about the electronic states. The existence of high fission barrier of multiply charged polycyclic aromatic hydrocarbons was investigated by using DFT theory [31]. For further investigation of the stability of multiply charged C_{10}F_8 , a large basis set and high-level treatment using multi-configurational method (e.g. multi-reference configuration interaction) is required at least [32]. However, such calculations are great challenges and beyond the scope of the present work. Although the definitive conclusion cannot be made, the charge delocalization over the naphthalene moiety determines the stability of multiply charged C_{10}H_8 and C_{10}F_8 . Coulomb explosion of H^+ promptly occurs if the adjacent carbon is partially charged in the case of C_{10}H_8 , whereas F^+ having much electrons than hydrogen could survive even

if the adjacent carbon is charged. In other word, positive charges can be localized on the fluorine atoms as in the case of iodine atoms in diiodoacetylene tetracation [23]. Another possible role of fluorine substitution is isomerization that can stabilize multiply charged states by increasing the distance between positive charges as suggested for C_6F_6 dication [33]. Experimentally, we expect that the use of the perfluoro-aromatics with enlarged π moiety would improve the pentacation radical yields.

4. Conclusion

Our findings satisfy the requirements for the definitive identification of multiply charged species especially of the pentacation radical of organic molecule for the first time. Although the yield of $C_{10}F_8^{5+}$ is two order of magnitude smaller than that of $C_{10}F_8^{4+}$, the lower limit of the lifetime of pentacation radical is estimated to be 11 μ s. MMCs that show prompt dissociation have been utilized as the precursor of Coulomb explosion imaging such as the determination of absolute stereochemistry of chiral molecules [34] as well as of the molecular structure deformation in intense laser fields [35]. The production of not only dication and trication radical but also tetracation and pentacation radical as intact MMCs widens the way to investigate the multiply charged cation chemistry such as the competition between the charge transfer and bond-forming

reactions [36-38], and spectroscopy, as well as provides the appropriate samples for theoretical considerations [32]. A series of perfluoro-aromatic MMCs is promising and suitable candidates for these challenges.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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