Formation and Fragmentation of Quadruply Charged Molecular Ions by Intense Femtosecond Laser Pulses

2 AUTHORS:

Tomoyuki Yatsuhashi
Osaka City University
64 PUBLICATIONS **908** CITATIONS

SEE PROFILE

Nobuaki Nakashima
Toyota Physical and Chemical Institute
214 PUBLICATIONS **4,160** CITATIONS

SEE PROFILE

Formation and Fragmentation of Quadruply Charged Molecular Ions by Intense Femtosecond Laser Pulses

Tomoyuki Yatsuhashi*,†,‡ and Nobuaki Nakashima†

Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585 Japan, and PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama, 332-0012 Japan

Received: April 26, 2010; Revised Manuscript Received: June 14, 2010

We investigated the formation and fragmentation of multiply charged molecular ions of several aromatic molecules by intense nonresonant femtosecond laser pulses of 1.4 μm with a 130 fs pulse duration (up to 2 $\times$ 10^{14} W cm^{-2}). Quadruply charged states were produced for 2,3-benzofluorene and triphenylene molecular ion in large abundance, whereas naphthalene and 1,1′-binaphthyl resulted only in up to triply charged molecular ions. The laser wavelength was nonresonant with regard to the electronic transitions of the neutral molecules, and the degree of fragmentation was strongly correlated with the absorption of the singly charged cation radical. Little fragmentation was observed for naphthalene (off-resonant with cation), whereas heavy fragmentation was observed in the case of 1,1′-binaphthyl (resonant with cation). The degree of H$_2$ (2H) and 2H$_2$ (4H) elimination from molecular ions increased as the charge states increased in all the molecules examined. A striking difference was found between triply and quadruply charged 2,3-benzofluorene: significant suppression of molecular ions with loss of odd number of hydrogen was observed in the quadruply charged ions. The Coulomb explosion of protons in the quadruply charged state and succeeding fragmentation resulted in the formation of triply charged molecular ions with an odd number of hydrogens. The hydrogen elimination mechanism in the highly charged state is discussed.

Introduction

The formation of highly charged atomic ions in the gas phase[1] is one of the interesting and attractive features of ionization with high-intensity laser, the electric fields of which are larger than those of valence electrons in atoms and molecules.[2] An extensive number of electrons is stripped out from rare gases[3] above 10^{18} W cm^{-2}, as in the case of the electron beam ion trap method.[4] An intact molecular ion[5] and the formation of its highly charged states is desirable not only for analytical applications[6] and new synthetic methods,[7] but also for fundamental studies.[8] C$_{60}^{12+}$ is the highest charge state ever observed for molecules experimentally (70 fs, 1.8 μm, 10^{15} W cm^{-2}),[9] and its stability was theoretically approved.[10] In contrast, a triply charged molecular ion is the highest charge state ever observed by femtosecond laser ionization for common hydrocarbons.[11] States with higher charge are generally not achieved because dissociation of the C−H bond occurs easily in these highly charged states. The hydrocarbons have many C−H bonds, and the dissociation energy of the specific C−H bond of a cation radical[12] is smaller than (around 0.33−0.77 times)[13] that of a neutral one. The presence of a relatively weak C−H bond prevents the formation of intact multiply charged hydrocarbons. In addition, most large molecules show heavy fragmentation with 0.8 μm pulses, even with low-intensity femtosecond laser pulses (10^{13} W cm^{-2}),[14] also making the formation of a highly charged state difficult. The importance of electronic excitation of radical cations in the postionization fragmentation process has been recognized, and controversy as to arguments regarding the fragmentation mechanism is ongoing.[15–17] Evidently, we can use shorter-duration pulses[18] and/or pulses at a suitable wavelength that is off-resonant with regard to the electronic transition of the molecular cation radicals to avoid fragmentation.[19] The effect of resonance in fragmentation process of anthracene cation radical has been investigated even with 40 fs pulses.[20] At comparable intensities above the saturation threshold for complete ionization, the fragmentation are enhanced with a circularly polarized light compared to a linearly polarized light. As the transition moment of anthracene cation radical locates along the short axis of anthracene, the circularly polarized field interacts with a larger fraction of the randomly oriented cations than the linearly polarized field and results in the enhanced fragmentation by circularly polarized light. A distinct wavelength effect was found in metal carbonyls by Trushin et al., with off-resonant but shorter wavelength pulses giving a molecular ion of Ni(CO)$_4$, but with longer and resonant wavelength pulses giving fragmentation.[21] Generally, an off-resonant longer wavelength pulse is better than an off-resonant shorter one to produce highly charged molecular ions.[22] The formation of highly charged ions is a specific feature in the gas phase. Even doubly charged molecular ions are missing in the solid phase under the same laser conditions.[23]

In this study, four organic molecules were irradiated with a 1.4 μm femtosecond high-intensity laser pulse. Ionization and fragmentation of naphthalene were compared with three molecules with naphthalene moieties. These included 2,3-benzofluorene, in which naphthalene and benzene were fused with a five-membered ring; triphenylene, in which naphthalene was fused with two benzene rings; and 1,1′-binaphthyl, in which two naphthalenes were connected with a single bond. We observed quadruply charged molecular ion of 2,3-benzofluorene and triphenylene. A quadruply charged molecular ion obtained

* To whom correspondence should be addressed. Telephone: +81-6-6605-2554. FAX: +81-6-6605-2522. E-mail: tomo@sci.osaka-cu.ac.jp.
† Osaka City University.
‡ Japan Science and Technology Agency.

by electron impact ionization has been reported for ovalene ($C_{32}H_{14}$) for the first time.[24] We observed a 1−4 orders of magnitude higher relative abundance of doubly, triply, and quadruply charged molecular ions compared with electron impact ionization, indicating that the femtosecond laser ionization method has a potential to produce highly charged molecular ions. The formation and fragmentation of highly charged states occurred simultaneously, except for naphthalene. In contrast to naphthalene, fragmentation occurred in the molecules whose cation radical absorption appeared at laser wavelength (1.4 μm). The fragmentation, at least singly charged ion, can again be simply explained by the resonance-induced fragmentation. The fragmentation of dications of organic molecule has been studied by the electron impact ionization method;[25] however, that of triply and higher charge states has rarely been studied.[26] We compared the degree of hydrogen elimination from highly charged molecules. As the charge state increased, the H_2 (2H) elimination became significant in all molecules examined. We found different degrees of hydrogen elimination depending on the charge states: significant suppression of molecular ions with loss of odd number of hydrogen was observed in quadruply charged 2,3-benzofluorene. The origin of a high abundance of triply charged molecular ion of 2,3-benzofluorenone with loss of odd number of hydrogen would be the Coulomb explosion of H^+ in the quadruply charged state followed by neutral H_2 elimination in the triply charged state. The high abundance of quadruply charged molecular ion of 2,3-benzofluorenone with loss of even number of hydrogen can be explained in the same manner: ions with loss of H_2 can keep their quadruple charge. The hydrogen elimination mechanism in the highly charged state is discussed herein.

Experimental Section

Naphthalene ($C_{10}H_8$, Nacalai, zone refined) was used as received. 2,3-Benzofluorene ($C_{17}H_{12}$, Tokyo Kasei, GR), triphenylene ($C_{18}H_{12}$, Nacalai, GR), and 1,1′-binaphthyl ($C_{20}H_{14}$, Tokyo Kasei, GR) was purified by sublimation. Xenon was purchased from Japan Air Gases with a stated purity of 99.99%. Xenon was introduced effusively by a leak valve. Naphthalene derivatives were heated (naphthalene, 296 K; 2,3-benzofluorene, 383 K; triphenylene, 403 K; 1,1′-binaphthyl, 378 K) and introduced effusively through a 1 mm ϕ aperture located 40 mm above the laser focus point. The base pressure of the ionization chamber and that of time-of-flight chamber were below 5×10^{-7} Pa. The sample pressure at the position 20 cm away from the laser focus point was monitored and kept below 5×10^{-5} Pa by adjusting heating temperature during the experiments to avoid a space-charge effect. The pressure in the time-of-flight mass chamber was kept to below 10 times that of the ionization chamber by differential pumping to avoid collision-induced dissociation. A 0.5 TW Ti:Sapphire laser (Thales laser, Alpha100/XS, < 30 fs, 100 Hz, > 15 mJ, 800 nm, rms stability ∼1%)[27] was used to excite an optical parametric amplifier. In this study, negative group velocity dispersions were introduced by the acoustoptic programmable dispersive filters (Fastlite, Dazzler) to have 100 fs pulse of Alpha100/XS and was used for pumping the optical parametric amplifier (Quantronix, TOPAS). A 1.4 μm pulse was selected by reflecting it with several dielectric mirrors. The pulse width was measured by a second-order scanning autocorrelator (APE, PulseCheck). The same optical elements, such as the ionization chamber window, focusing lens, and neutral density filter, were placed in front of the autocorrelator to have the same group velocity dispersion. A pulse of 130 fs duration was used for the experiments.

A reflectron-type time-of-flight mass spectrometer (Toyama, KNTOF-1800, flight length: 1.8 m) was used for ion analysis. An aperture of 10 mm diameter was located on the extraction plate. The output signal from a MCP was averaged by a digital oscilloscope (LeCroy, Wave Runner 6100, 1 GHz) for 1000 shots. A weak signal was amplified by a fast preamplifier (Phillips Scientific 6954, 1.8 GHz, gain 10). The ion yield was obtained by integrating over the appropriate peaks in the time-of-flight spectrum. For determining hydrogen contents in molecular ion, multiple peak fitting with several Gaussian shape was performed. The resolution ($m/\Delta m$, fwhm) was more than 10^3 at $m/z = 129$.

The direction of laser polarization was orthogonal to the time-of-flight axis. The laser light was focused into the ionization chamber with a plano-convex quartz lens with a 200 mm focusing length. The position of the lens was adjusted to maximize the intensity of the doubly charge state of xenon. The laser energy was attenuated by a reflection-type neutral density filter (Sigma Koki), and average laser power was measured by a power meter. The actual laser intensity of the linear polarization pulse at the focus was determined by measuring the saturation intensity (I_{sat}) of xenon using the method of Hankin et al.[28] I_{sat} of xenon was 9.3×10^{13} W cm^{-2} (130 fs; ADK (Ammosov-Delone-Krainov) value was multiplied by 1.12 for adjusting to the experimental value[28]).

Results and Discussion

Multiply Charged Molecular Ion Formation by Femtosecond Laser Pulses. Figure 1 shows the time-of-flight mass spectra ionized using 1.4 μm pulses. The spectral regions of singly, doubly, triply, and quadruply charged molecular ions are magnified. M^{z+} denotes the zth charged molecular ion, whereas they should be written as $M^{+\bullet}$, M^{2+}, $M^{3+\bullet}$, and M^{4+}, respectively. A quadruply charged molecular ion was observed for 2,3-benzofluorene and triphenylene. A multiply charged molecular ion was definitively identified by a noninteger number of isotope peaks, a narrower peak width than that of lower charged ions, and a peak intensity ratio. For example, a quadruply charged molecular ion of 2,3-benzofluorene (Figure 1b) appeared at $m/z = 54$, and its isotope peak appeared at $m/z = 54.25$. The peak intensities (or integrated areas) were in agreement with the calculated isotope ratio. A quadruply charged molecular ion obtained by electron impact ionization has been reported for ovalene ($C_{32}H_{14}$) for the first time.[24] Ovlalene is a large polycyclic aromatic hydrocarbon that has a fused structure of 10 benzene rings, thus allowing the delocalization of multiple charges. Quadruply charged aromatic molecules larger than anthracene obtained by electron impact ionization have also been reported; however, the relative abundance of quadruply charged molecular ions was quite small.[29] The relative abundances of multiply charged molecular ions compared with singly charged ions are summarized in Table 1. The relative ion yields of naphthalene and triphenylene are compared with those obtained by electron impact ionization.[29] The relative yield of quadruply charged ion of triphenylene was 14 000 times larger than that obtained by electron impact ionization. We believe this to be the first case of successful formation of a high abundance of quadruply charged molecular ions. There is no doubt that femtosecond laser ionization has a potential to produce highly charged molecular ions.

In the case of naphthalene, the mass spectrum was very simple, and the triply charged molecular ion, the highest charge state of naphthalene, was clearly observed with little fragmentation. It is quite significant that H^+ was not observed by 1.4 μm
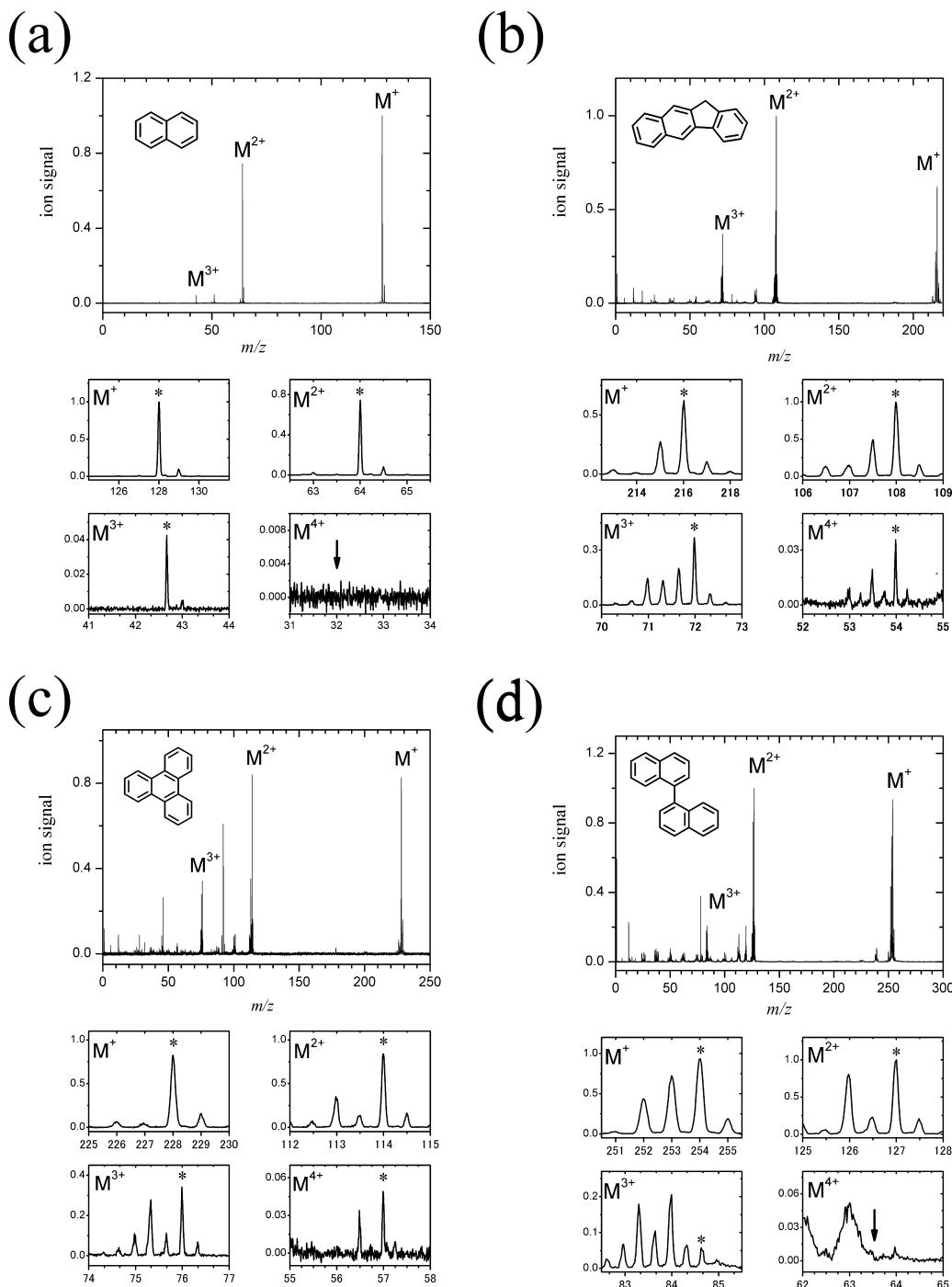
Formation and Fragmentation of Multiply Charged Ions

J. Phys. Chem. A, Vol. 114, No. 28, 2010 **7447**

Figure 1. Time-of-flight mass spectra of (a) naphthalene, (b) 2,3-benzofluorene, (c) triphenylene, and (d) 1,1′-binaphthyl ionized by 1.4 μm pulse. Laser intensities are (a) 1.3×10^{14} W cm^{-2}, (b) 2.0×10^{14} W cm^{-2}, (c) 2.1×10^{14} W cm^{-2}, and (d) 1.4×10^{14} W cm^{-2}, respectively. Symbol M^{z+} indicates the zth charged molecular ion. The lower panels show the magnification of the same spectrum. Asterisks indicate M^{z+}. The arrow indicates the expected position of the quadruply charged molecular ion (M^{4+}) if it does not appear.

TABLE 1: Relative Abundance of Highly Charged Molecular Ion Yields[a]

	M$^+$	M^{2+}	M^{3+}	M^{4+}	laser intensity (10^{14} W cm^{-2})
naphthalene	1	0.46	0.023	[b]	1.3
naphthalene	1	0.04	4×10^{-5}	[b]	electron impact[c]
2,3-benzofluoroene	1	1.1	0.31	0.025	2.0
triphenylene	1	0.69	0.21	0.041	1.8
triphenylene	1	0.07	4×10^{-3}	3×10^{-6}	electron impact[c]
1,1′-binaphthyl	1	0.82	0.45	[b]	1.5

[a] Detector sensitivity was not corrected. [b] Not observed. [c] Relative ion current produced by electron impact ionization (70 eV). Reference 29.

ionization, whereas there was dominant production of H$^+$ in the case of 0.8 μm ionization.[19] We have reported that the major

fragments of naphthalene by 1.4 μs pulses were C$_2$H$_2$$^+$ and the ion of $m/z = 51$, which was assigned as (M-C$_2$H$_2$)$^{2+}$ in the high-
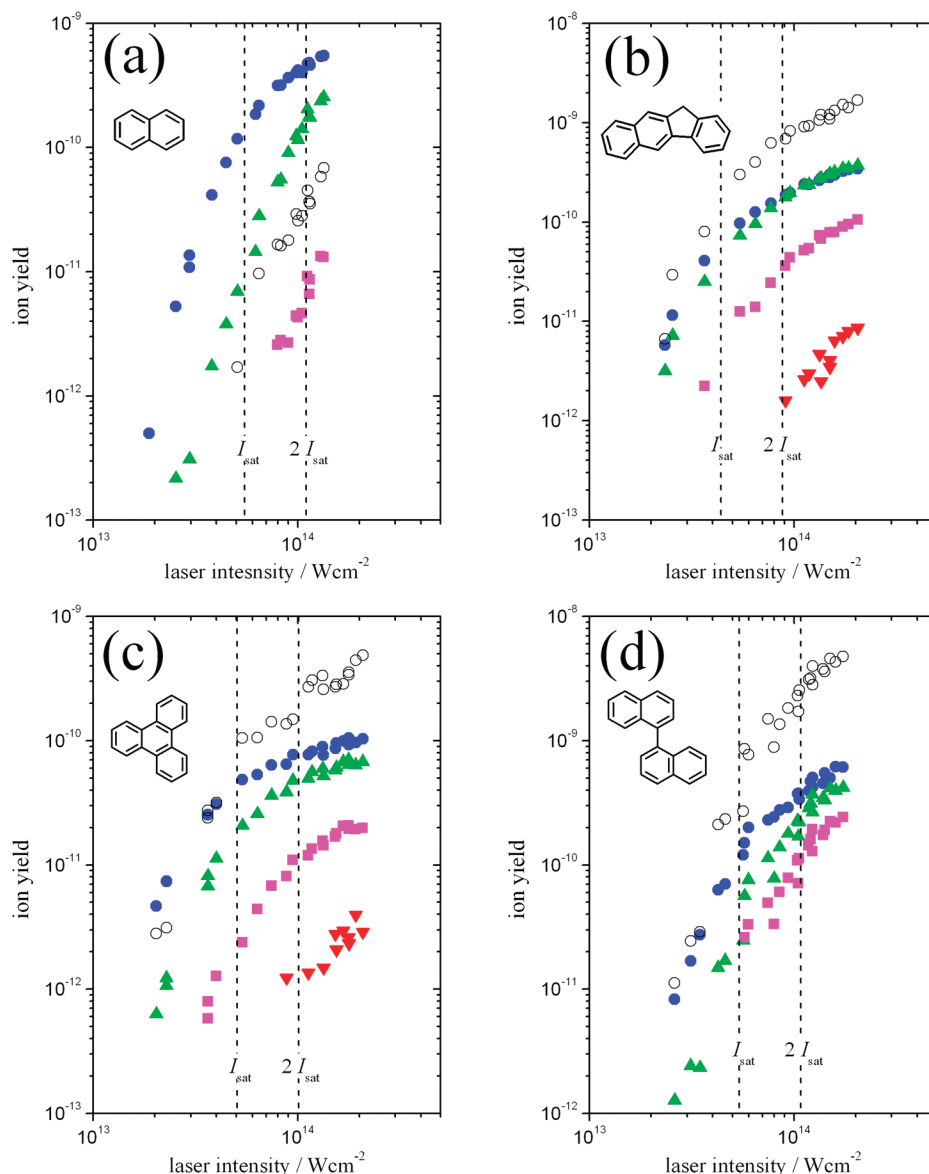
Figure 2. Ion yields of (a) naphthalene, (b) 2,3-benzofluorene, (c) triphenylene, (d) 1,1′-binaphthyl as a function of laser intensity: M^+ (•); M^{2+} (▲); M^{3+} (■); M^{4+} (▼); Fragments (°). I_{sat} and $2I_{sat}$ are indicated by dashed lines.

intensity region.[30] $(M-C_2H_2)^{z+}$ denotes the zth charged molecular ion with loss of acetylene. In contrast to naphthalene, fragmentation was obvious for other molecules. The fragment ions of 2,3-benzofluorene ($C_{17}H_{12}$) were assigned to be $C_nH_m^+$ ($n = 1-8$), $C_nH_m^{2+}$ ($n = 13, 15, 17$), and $C_{17}H_m^{3+}$. Triphenylene ($C_{18}H_{12}$) showed $C_nH_m^+$ ($n = 1-6$), $C_nH_m^{2+}$ ($n = 14, 16, 18$), and $C_{18}H_m^{3+}$. The existence of other $C_nH_m^{3+}$ was not certain due to the low-intensity ion signals and spectral overlap with ions of lower charge states. 1,1′-Binaphthyl ($C_{20}H_{14}$) showed violent fragmentation compared with other derivatives: $C_nH_m^+$ ($n = 1-20$), $C_nH_m^{2+}$ ($n = 15-20$), and $C_nH_m^{3+}$ ($n = 18-20$) were observed.

Large mass fragments with loss of carbon dominantly appeared not as singly nor triply charged ions but as doubly charged ions, except for 1,1′-binaphthyl. Although there were several doubly charged fragments with loss of carbons and with different hydrogen contents, we will mention only the largest peak among the doubly charged fragments with a specified number of carbons. $C_{15}H_9^{2+}$ and $C_{13}H_7^{2+}$ were formed by the expulsion of C_2H_3 and C_4H_5 in the case of 2,3-benzofluorene. $C_{16}H_{10}^{2+}$ and $C_{14}H_8^{2+}$ were formed by the expulsion of C_2H_2

and C_4H_4 in the case of triphenylene. The successive C_2 fragmentation processes, possibly as C_2H_2, seemed to be dominant in doubly charged molecular ions in those molecules. In contrast, 1,1′-binaphthyl, the expulsion of CH_3, C_2H_4, C_3H_5, C_4H_6, and C_5H_7 resulted in $C_{19}H_{11}^{2+}$, $C_{18}H_{10}^{2+}$, $C_{17}H_9^{2+}$, $C_{16}H_8^{2+}$, and $C_{15}H_7^{2+}$ formation. Triply charged fragments with loss of carbon were observed only for 1,1′-binaphthylene, but molecular ions with loss of hydrogen were observed in any of the charged states for all the molecules examined. We will therefore discuss the fragmentation from highly charged states, giving specific attention to the hydrogen atom content, later.

Resonance-Induced Fragmentation of Molecular Ions. Figure 2 shows the laser intensity dependencies of the yields of molecular ions as well as the total number of fragment ions. We used the saturation intensity (I_{sat}) proposed by Hankin et al.,[28] to quantitatively evaluate the degree of ionization. I_{sat} corresponds to the intensity at a certain ionization probability and is defined as the point at which the ion yield (linear scale), extrapolated back from the high-intensity linear portion of the curve, intersects the intensity axis (logarithmic scale). The I_{sat} values for the sum of molecular ions were 5.5×10^{13}
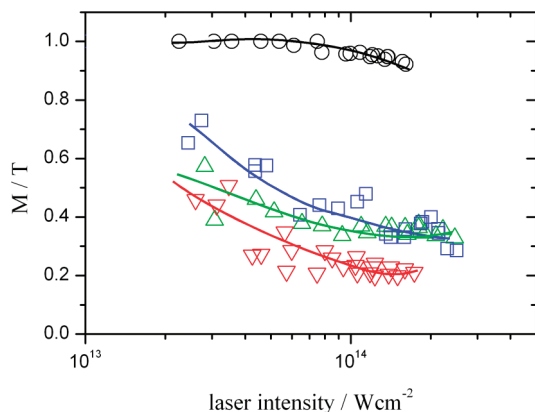
Formation and Fragmentation of Multiply Charged Ions

J. Phys. Chem. A, Vol. 114, No. 28, 2010 **7449**

Figure 3. Ratio of the sum of molecular ions of all charge states (*M*) to total ions (*T*) including all charge states of molecular ions and fragment ions: naphthalene (○); 2,3-benzofluorene (△); triphenylene (□); 1,1′-binaphthyl (▽). Solid lines are given to show the tendency.

Figure 4. Absorption spectra of the cation of naphthalene (solid line), 2,3-benzofluorene (dotted line), triphenylene (bold line), 1,1′-binaphthyl (dashed line) in a low-temperature rigid matrix. The spectra were taken from the literature,[33] with permission from Elsevier. The excitation laser wavelength (1.4 μm) is indicated by an arrow and dashed line.

(naphthalene), 4.4×10^{13} (2,3-benzofluorene), 5.1×10^{13} (triphenylene), and 5.4×10^{13} W cm^{-2} (1,1′-binaphthyl), respectively. I_{sat} values are indicated in Figure 2. The vertical ionization potential of naphthalene, 2,3-benzofluorene, and triphenylene are 8.15,[31] 7,[12] and 7.88[32] eV, respectively. It would therefore be reasonable to give similar I_{sat} values for all derivatives. A characteristic difference appeared not for ionization process itself but for fragment ion formation.

Naphthalene showed almost fragment-free ionization, whereas other naphthalene derivatives showed heavy fragmentation. The most of fragment ions were singly charged. Figure 3 shows the ratio of the sum of molecular ions of all charge states (*M*) to total ions (*T*), including all charge states of molecular ions and fragment ions. *M/T* values at I_{sat} were 1.0 (naphthalene), 0.38 (2,3-benzofluorene), 0.47 (triphenylene), and 0.25 (1,1′-binaphthyl), respectively. We have reported strong suppression of fragmentation by using a 1.4 μm pulse instead of a 0.8 μm pulse in the case of naphthalene.[30] The dominance of molecular ions of naphthalene was explained well in terms of nonresonance with regard to the electronic transition of the cation radical as in the case of anthracene:[19] the naphthalene cation radical does not have absorption at 1.4 μm but it does at 0.8 μm. Figure 4 shows the absorption spectra of the related cation in a low-temperature rigid matrix taken from the literature.[33] Except for naphthalene, characteristic absorption appeared longer than 1 μm. Unfortunately, information about the molar extinction coefficient was missing. Assuming that absorption appearing between 600 and 750 nm had the same origin and that the absorption coefficients of characteristic peaks were the same for all derivatives, the order of absorbency became 1,1′-binaphthyl > 2,3-benzofluorene = triphenylene ≫ naphthalene. It appears that there was qualitative agreement between absorbency and the degree of fragmentation as in the case of ketones.[34] The lower charge states are formed at the leading edge of laser pulse and has plenty chance to absorb photons. Higher charge states are formed at the peak of laser pulse where laser intensity is maximum, thus still having a chance to absorb photons at the trailing edge of laser pulse. In both cases, accumulation of excess energy by repeated photoabsorption and relaxation is possible due to the longer laser pulse (130 fs). We expect that both ground and excited states of highly charged molecules are unstable in nature. They will decompose by hydrogen elimination, which needs less activation energy, with certain probability. Excitation by a single photoabsorption process will greatly increase the reaction rate. However, most
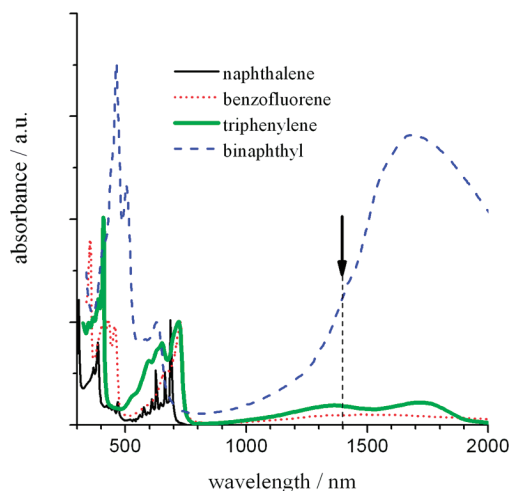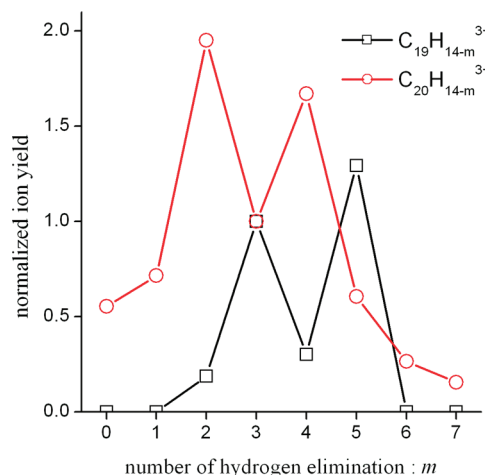

Figure 5. Ion yields of 1,1′-binaphthyl $C_{20}H_{14-m}^{3+}$ and $C_{19}H_{14-m}^{3+}$ as a function of the number of hydrogen eliminations *m*: ion yields are normalized by *m* = 3.

fragment ions were singly charged, and the fragments with loss of carbon were not observed for the quadruply charged state. Triply charged fragments with loss of carbon was only observed for 1,1′-binaphtyl. No complete interpretation can be formulated, because the absorption spectra of higher charge states are not known. It is not unreasonable that the absorption of highly charged states shifts to shorter wavelength region[35] than that of monocation because the energies of occupied orbital are expected to be lowered and the gaps to be widened. The absorption at the excitation wavelength of 1.4 μm could be low for highly charged ions.

Carbon Elimination from Highly Charged Molecular Ions. Fragmentation of dications of organic molecules has been studied by electron impact ionization mass spectroscopy, especially through the use of photoion photoelectron coincidence measurements;[25] however, triply and higher charge states have rarely been studied. Femtosecond laser ionization is an ideal method for the production of highly charged molecular ions. However, the observation of $C_nH_m^{3+}$ and $C_nH_m^{4+}$ was limited to some extent. Quadruply charged ions with loss of carbon were not observed for all the molecules examined. Triply
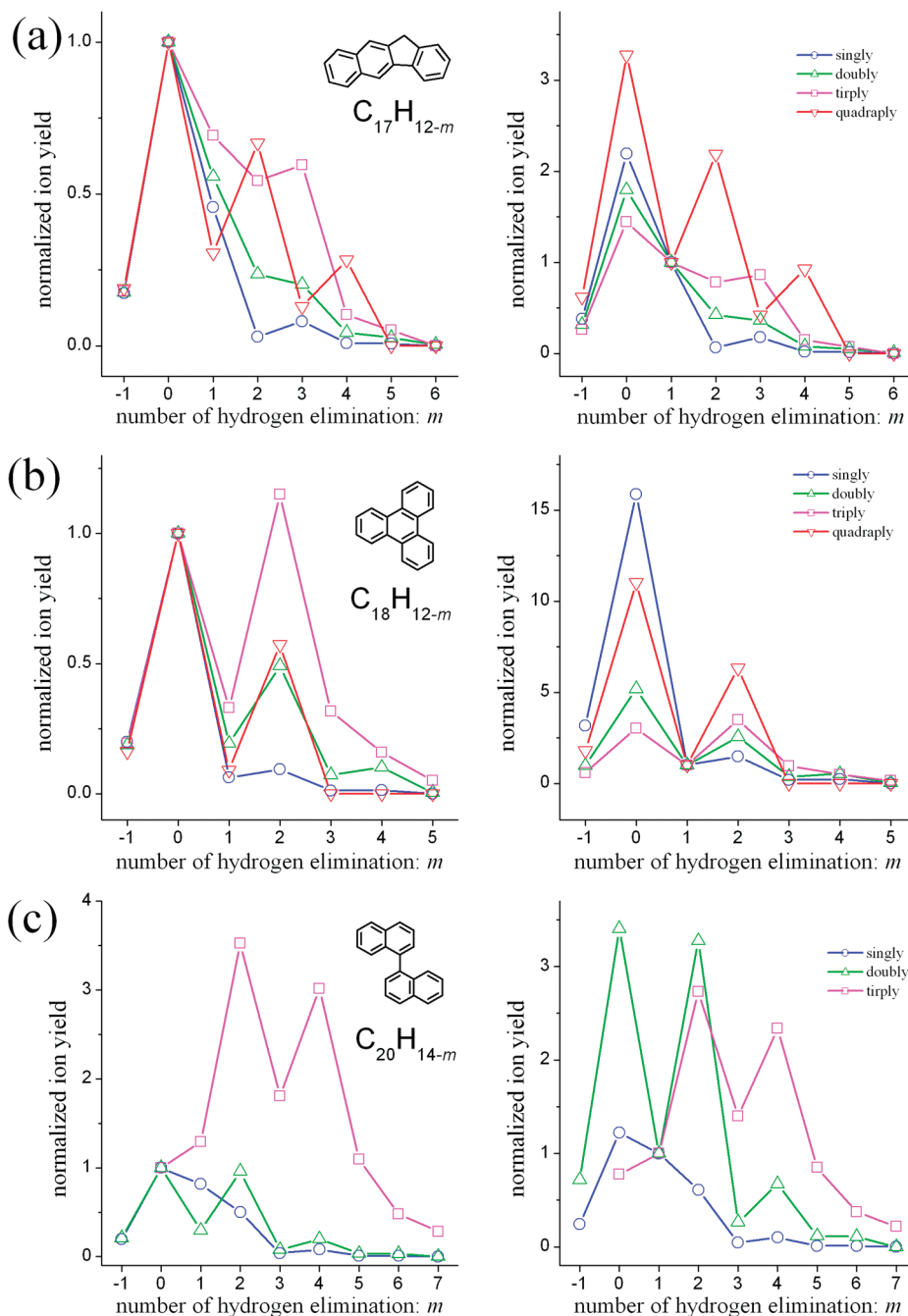
Figure 6. Ion yields of $(M - mH)^{z+}$ as a function of the number of hydrogen eliminations m: Ion yields were normalized by M^{z+} (left panels) and by $(M-H)^{z+}$ (right panels), respectively. (a) 2,3-benzofluorene; (b) triphenylene; (c) 1,1′-binaphthyl: $z = 1$ (○); $z = 2$ (△); $z = 3$ (□); $z = 4$ (▽).

charged fragments with loss of carbon were identified in 1,1-binaphthlene ($C_nH_m^{3+}$, $n = 18-19$), but we can measure the degree of hydrogen elimination precisely only for $C_{19}H_{14-m}^{3+}$ ($m = 2-5$) and molecular ion of $C_{20}H_{14-m}^{3+}$ ($m = 0 -7$) due to the low intensity of ions and overlap with doubly charged fragments. The fragmentation patterns were independent of the laser intensity above I_{sat} in all charge states. Figure 5 shows the ion yields of $C_{19}H_{14-m}^{3+}$ and $C_{20}H_{14-m}^{3+}$ from 1,1′-binaphthyl as a function of the number of hydrogen eliminations m. Ion yields were normalized at $m = 3$. The relative abundance of ion yields were different between C_{19} and C_{20} ions. The even number of hydrogen eliminations were significant in the case of C_{20}, whereas an odd number of hydrogen was dominantly eliminated in the case of C_{19}. The reason for this opposite tendency would be the fragmentation proceeded by the elimina-

tion of carbon accompanying odd number of hydrogen. For example, several combinations are possible for $m = 3$ (H + CH_2, $H_2 + CH$, CH_3). A similar comparison for doubly charged ions was difficult due to the spectral overlap with singly charged fragments.
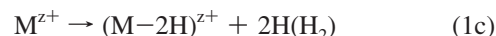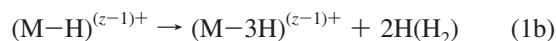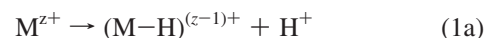
Hydrogen Elimination from Highly Charged Molecular Ions. There were small but many fragment ions with loss of carbon; however, the dominant fragment ions originated from hydrogen elimination from molecular ions in each of the charge states, as judged from the mass spectra (Figure 1). For the cases of ions with loss of carbon, the spectral overlap with lower charge state ions created ambiguities in the quantitative analysis. In contrast, we can definitively compare the hydrogen atom content (i.e., degree of hydrogen elimination) of molecular ions for all charge states without ambiguity and thus discuss the

Formation and Fragmentation of Multiply Charged Ions

J. Phys. Chem. A, Vol. 114, No. 28, 2010 **7451**

stability and reactivity of highly charged molecular ions. The acceleration time in the time-of-flight mass spectrometer was shorter than 1 μs; the ions should therefore have been detected at a certain m/z if they were stable and reaction rate of the precursor ions was higher than 10^6 s^{-1}. In addition, no fragments appeared at irregular values of m/z, indicating that there was no fragmentation in the field-free region. Figure 6 shows the ion yields of $(M - mH)^{z+}$ as a function of the number of hydrogen eliminations m. Ion yields normalized by that of M^+ are shown in the left panels of Figure 6. It should be noted first that the observed ion yield ratios between M^+ and $(M + H)^+$ were the same as those predicted by the isotope ratio and that the ratios were independent of the charge states. These two results strongly support the observation of molecular ions for all charges states.

To compare the elimination of hydrogen and H$_2$ (2H), the ion yields were normalized by that of $(M - H)^{z+}$ in the right panels of Figure 6. As the charge state increased, the production of $(M - 2H)^{z+}$ was clearly increased in all molecules examined except for 1,1′-binaphthyl. The relative yield of H$_2$ elimination was similar between doubly to triply charged 1,1′-binaphthyl; however, the elimination of 2H$_2$ was increased by a factor of 3.5 in triply charged state compared with that in doubly charged state. Successive elimination of H$_2$ (2H) should be a very important fragmentation process in 1,1′-binaphthyl. The elimination of 2H$_2$ was also observed significantly in the quadruply charged 2,3-benzofluorene. The hydrogen and H$_2$ elimination was the dominant fragmentation process; however, the yield of H$^+$ was very small. We can see small but not negligible amounts of H$^+$, C$^+$, and C^{2+} under the high-intensity condition in the cases of 2,3-benzofluorene, triphenylene, and 1,1′-binaphthlene. In addition, peak splitting was observed in H$^+$ and C^{2+}. The origin of the peak splitting appeared to be the Coulomb explosion (charge separation processes) of fragment ions; the ions' forward and backward emissions against the flight axis.[36] It can therefore be concluded that the Coulomb explosion process contributes to the hydrogen elimination process. The low abundance of H$^+$ formation was strikingly different from the 0.8 μm pulse ionization reported for anthracene.[19] With a 0.8 μm pulse, the production of H$^+$ and multiply charged carbon ions by Coulomb explosion was significant.

The degree of H$_2$ and 2H$_2$ elimination from molecular ions increased as the charge states increased in all the molecules examined. However, significant suppression of molecular ions with loss of odd number of hydrogen was observed in quadruply charged 2,3-benzofluorene (Figure 6a). In addition, the abundance of hydrogen elimination showed opposite tendencies between triply and quadruply charged molecular ions (Figure 6a). The odd number of hydrogen (H, 3H) elimination was significant in singly, doubly, and triply charged ion, whereas even numbers of hydrogen (2H, 4H) were dominantly eliminated in quadruply charged ion. The difference in fragmentation between quadruply charged ions and the lower charge ion might be explained by the contribution of Coulomb explosion (Scheme 1). Singly (triply) charged radical ions have an odd number of electrons, whereas doubly (quadruply) charged ions have either no or two unpaired electrons. A Coulomb explosion forming two odd electron products would be expected in the latter case. Coulomb explosion of H$^+$ would be very fast (within the laser pulse duration). The origin of a high abundance of triply charged fragments with loss of odd number of hydrogen (H, 3 H) would be a Coulomb explosion of H$^+$ in the quadruply charged state (Scheme 1a) followed by neutral H$_2$ elimination in the triply charged state (Scheme 1b). A high abundance of quadruply

SCHEME 1: Fragmentation Processes: (a) Coulomb explosion of zth charged molecular ion, (b) 2H elimination from $(z-1)$th charged ion, (c) 2H (H$_2$) elimination from zth charged molecular ion

$$M^{z+} \rightarrow (M-H)^{(z-1)+} + H^+ \qquad (1a)$$

$$(M-H)^{(z-1)+} \rightarrow (M-3H)^{(z-1)+} + 2H(H_2) \qquad (1b)$$

$$M^{z+} \rightarrow (M-2H)^{z+} + 2H(H_2) \qquad (1c)$$

charged molecular ions with loss of even number of hydrogen can be explained in the same manner: ions with loss of H$_2$ can maintain their quadruple charge (Scheme 1c). The reason of weak H$^+$ signal in the mass spectra can also be explained in terms of H$^+$ production in quadruply charged state. The specific difference in 2,3-benzofluorene may come from the existence of a methylene part.

In our measurements, we were unable to determine whether the detailed elimination mechanisms were successive or concerted. In addition, it was quite difficult to identify the structures of fragment species due to the large number of possible structures. In addition, the rearrangement reaction should be considered. The detailed photofragmentation mechanism of singly charged 2,3-benzofluorene was investigated by mass-selective photolysis with Fourier transform ion cyclotron resonance mass spectroscopy.[37] Two hydrogen eliminations proceeding by either successive (2H, major) or concerted (H$_2$, minor) pathways were found. Hydrogen elimination followed by H$_2$ and C$_2$H$_2$ elimination was the major fragmentation process of singly charged molecular ions of 2,3-benzofluorene. Investigation of the hydrogen elimination mechanism in a mass-selected highly charged state would be very interesting. We found different degrees of hydrogen elimination depending on the charge states, but further theoretical calculations regarding the stability of highly charged ions as well as spectroscopic properties are required for elucidation of fragmentation processes.

References and Notes

(1) Chin, S. L.; Rolland, C.; Corkum, P. B.; Kelly, P. *Phys. Rev. Lett.* **1988**, *61*, 153.

(2) Levis, R. J.; DeWitt, M. J. *J. Phys. Chem. A* **1999**, *103*, 6493. Nakashima, N.; Shimizu, S.; Yatsuhashi, T.; Sakabe, S.; Izawa, Y. *J. Photochem. Photobiol. C* **2000**, *1*, 131.

(3) Yamakawa, K.; Akahane, Y.; Fukuda, Y.; Aoyama, M.; Inoue, N.; Ueda, H.; Utsumi, T. *Phys. Rev. Lett.* **2004**, *92*, 123001.

(4) Marrs, R. E.; Elliott, S. R.; Knapp, D. A. *Phys. Rev. Lett.* **1994**, *72*, 4082. Currell, F. J., Ed. *The Physics of Multiply and Highly Charged Ions*; Kluwer Academic Pub.: Dordrecht, 2003; Vol. 1.

(5) DeWitt, M. J.; Levis, R. J. *J. Chem. Phys.* **1995**, *102*, 8670.

(6) Matsumoto, J.; Lin, C.-H.; Imasaka, T. *Anal. Chem.* **1997**, *69*, 4524. Shimada, Y.; Mizoguchi, R.; Shinohara, H.; Yatsuhashi, T.; Nakashima, N. *Bunseki Kagaku* **2005**, *54*, 127.

(7) Roithová, J.; Schröder, D. *J. Am. Chem. Soc.* **2006**, *128*, 4208.

(8) Ledingham, K. W. D.; Singhal, R. P.; Smith, D. J.; McCanny, T.; Graham, P.; Kilic, H. S.; Peng, W. X.; Wang, S. L.; Langley, A. J.; Taday, P. F.; Kosmidas, C. *J. Phys. Chem. A* **1998**, *102*, 3002.

(9) Bhardwaj, V. R.; Corkum, P. B.; Rayner, D. M. *Phys. Rev. Lett.* **2003**, *91*, 203004.

(10) Sahnoun, R.; Nakai, K.; Sato, Y.; Kono, H.; Fujimura, Y.; Tanaka, M. *Chem. Phys. Lett.* **2006**, *460*, 167. Sahnoun, R.; Nakai, K.; Sato, Y.; Kono, H.; Fujimura, Y.; Tanaka, M. *J. Chem. Phys.* **2006**, *125*, 184306.

(11) Ledingham, K. D. W.; Smith, D. J.; Singhal, R. P.; McCanny, T.; Graham, P.; Kilic, H. S.; Peng, W. X.; Langley, P. F.; Taday, P. F.; Kosmidis, C. *J. Phys. Chem. A* **1999**, *103*, 2952.

(12) Banisaukas, J.; Szczepanski, J.; Vala, M.; Hirata, S. *J. Phys. Chem. A* **2004**, *108*, 3713.

(13) Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1992**, *114*, 9787.

(14) Nakashima, N.; Yatsuhashi, T.; Murakami, M.; Mizoguchi, R.; Shimada, Y. In *Advances in Multiphoton Processses and Spectroscopy*; Lin, S. H.; Villaeys, A. A.; Fujimura, Y., Eds.; World Scientific Pub. Co Inc: Singapore, 2006; Vol. 17, p 179. Nakashima, N.; Yatsuhashi, T. In *Progress in Ultrafast Intense Laser Science II*; Yamanouchi, K.; Chin, S. L.; Agostini, P.; Ferrante, G., Eds.; Springer: Berlin, 2007; p 25.

(15) Harada, H.; Shimizu, S.; Yatsuhashi, T.; Sakabe, S.; Izawa, Y.; Nakashima, N. *Chem. Phys. Lett.* **2001**, *342*, 563. Harada, H.; Tanaka, M.; Murakami, M.; Shimizu, S.; Yatsuhashi, T.; Nakashima, N.; Sakabe, S.; Izawa, Y.; Tojo, S.; Majima, T. *J. Phys. Chem. A* **2003**, *107*, 6580. Tanaka, M.; Kawaji, M.; Yatsuhashi, T.; Nakashima, N. *J. Phys. Chem. A* **2009**, *113*, 12056.

(16) Markevitch, A. N.; Romanov, D. A.; Smith, S. M.; Schlegel, H. B.; Ivanov, M. Yu.; Levis, R. J. *Phys. Rev. A* **2004**, *69*, 013401.

(17) Robson, L.; Ledingham, K. W. D.; Tasker, A. D.; McKenna, P.; McCanny, T.; Kosmidas, C.; Jaroszynski, D. A.; Jones, D. R.; Lssac, R. C.; Jamieson, S. *Chem. Phys. Lett.* **2002**, *360*, 382.

(18) Campbell, E. E. B.; Hansen, K.; Hoffmann, K.; Korn, G.; Tchaplyguine, M.; Wittmann, M.; Hertel, I. V. *Phys. Rev. Lett.* **2000**, *84*, 2128. Tanaka, M.; Panja, S.; Murakami, M.; Yatsuhashi, T.; Nakashima, N. *Chem. Phys. Lett.* **2006**, *427*, 255.

(19) Murakami, M.; Mizoguchi, R.; Shimada, Y.; Yatsuhashi, T.; Nakashima, N. *Chem. Phys. Lett.* **2005**, *403*, 238.

(20) Murakami, M.; Tanaka, M.; Yatsuhashi, T.; Nakashima, N. *J. Chem. Phys.* **2007**, *126*, 104304.

(21) Trushin, S. A.; Fuβ, W.; Schmid, W. E. *J. Phys. B* **2004**, *37*, 3987.

(22) Lezius, M.; Blanchet, V.; Rayner, D. M.; Villeneuve, D. M.; Stolow, A.; Ivanov, M. Yu *Phys. Rev. Lett.* **2001**, *86*, 51. Lezius, M.; Blanchet, V.; Ivanov, M. Yu.; Stolow, A. *J. Chem. Phys.* **2002**, *117*, 1575. Smits, M.; de Lange, C. A.; Stolow, A.; Rayner, D. M. *Phys. Rev. Lett.* **2004**, *93*, 203402. Smits, M.; de Lange, C. A.; Stolow, A.; Rayner, D. M. *Phys. Rev. Lett.* **2004**, *93*, 213003.

(23) Yatsuhashi, T.; Nakashima, N. *J. Phys. Chem. A* **2008**, *112*, 5781. Yatsuhashi, T.; Nakashima, N. *J. Phys. Chem. C* **2009**, *113*, 11458.

(24) Bursey, Maurice, M.; Rogerson, Peter, F.; Bursey, Joan, M. *Org. Mass Spectrom.* **1970**, *4*, 615.

(25) Leach, S.; Eland, J. H. D.; Price, S. D. *J. Phys. Chem.* **1989**, *93*, 7575.

(26) Bruce, M. I. *Chem. Commun.* **1967**, 593.

(27) Yatsuhashi, T.; Obayashi, T.; Tanaka, M.; Murakami, M.; Nakashima, N. *J. Phys. Chem. A* **2006**, *110*, 7763.

(28) Hankin, S. M.; Villeneuve, D. M.; Corkum, P. B.; Rayner, D. M. *Phys. Rev. A* **2001**, *64*, 013405.

(29) Kingston, R. G.; Guilhaus, M.; Brenton, A. G.; Beynon, J. H. *Org. Mass Spectrom.* **1985**, *20*, 406.

(30) Yatsuhashi, T.; Nakashima, N. *J. Phys. Chem. A* **2005**, *109*, 9414.

(31) Tobita, S.; Leach, S.; Jochims, H. W.; Ruͨhl, E.; Illenberger, E.; Baumgärtel, H. *Can. J. Phys.* **1994**, *72*, 1060.

(32) Shushan, B.; Boyd, R. K. *Org. Mass Spectrom.* **1980**, *15*, 445.

(33) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: NewYork, 1988.

(34) Wu, D.; Wnag, Q.; Cheng, X.; Jin, M.; Li, X.; Hu, Z.; Ding, D. *J. Phys. Chem. A* **2007**, *111*, 9494.

(35) Malloci, G.; Mulas, G.; Cappellini, G.; Joblin, C. *Chem. Phys.* **2007**, *340*, 43.

(36) Yatsuhashi, T.; Murakami, M.; Nakashima, N. *J. Chem. Phys.* **2007**, *126*, 194316.

(37) Banisaukas, J.; Szezepanski, J.; Eyler, J.; Vala, M. *J. Phys. Chem. A* **2004**, *108*, 3723.