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Abstract

The kinetic energy of ions produced by a Coulomb explosion, in which multiply charged molecular cations dissociate, is determined by the charge number, mass, and geometric configuration of the ions upon explosion. Although the importance of the structural deformation and migration of atoms on kinetic energy variations is well known, there has been little investigation into the effect of charge localization before the ions are released. In this study, the angular distributions of iodine and carbon ions ejected from linear alkanes, which have one iodine atom on each side of an alkyl chain having one to six carbon atoms, are measured. The highly charged iodine ions (I^{4+} , I^{5+}) are emitted mostly along the laser polarization direction, whereas the angular distribution of iodine ions becomes isotropic the longer the alkyl chain and the lower the charge number of iodines are. Furthermore, the longer the alkyl chain, the higher the kinetic energy of iodine and carbon ions. The emission of ions is discussed in terms of the selective ionization of aligned molecules based on their molecular orbitals. The charge localization during ionization in strong alternating electric fields followed by two-body Coulomb explosion via a C–I bond cleavage is proposed.

Keywords

charge localization; field ionization; multiply charged molecular cations; mass spectrometry

1. Introduction

Coulomb explosions, which are destructive dissociations into atomic ions due to the strong Coulomb repulsion of positive charges, are one of the characteristic phenomena of multiply charged molecular cations (MMCs) in the gas phase [1, 2]. Coulomb explosion imaging is currently utilized to determine static molecular structures as well as to trace the molecular dynamics of ultrafast chemical reactions [3-8]. MMCs are produced by collision with high-energy projectiles such as Xe^{20+} , which is generated in an electron cyclotron resonance ion source [9]. MMCs are also produced by multiple ionization with ultrashort intense laser pulses in visible, near-infrared, and X-ray wavelength regions [10, 11]. The significant difference between these MMC production methods is the generation rate of the MMCs. The instantaneous generation (<1 fs) of MMCs is expected for a collision with projectiles, whereas that occurs within the pulse width for laser ionization. This difference results in different products and different kinetic energies of fragment

ions. For example, atomic ions such as C^{2+} and C^{3+} are dominant species formed from acetylene by intense femtosecond laser ionization [12], whereas, C_2H^+ and C_2^+ are also formed by collision with projectiles [13]. The absence of C_2H^+ and C_2^+ in laser ionization is attributed to the fact that the production of MMCs occurs at bond lengths greater than the equilibrium bond lengths, namely enhanced ionization [14, 15]. The Coulomb explosion dynamics of ions are strongly affected by their properties, such as the charge number, mass, and initial geometric configuration in MMCs. In addition, structural deformation [16] and the migration of atoms [17] before the Coulomb explosion should be considered for MMCs in a strong electric field. Moreover, nonequilibrium distribution of electrons (positive charges) in MMCs is expected during ionization, since the strong alternating electric fields shake the electrons in molecules [18, 19]. The localization of highly charged atomic ions on the edges of the molecular frame during ionization has been demonstrated by molecular dynamics simulation for benzenes [20, 21] and fullerenes [22]. The kinetic energy measurement of protons ejected from anthracene has also proved the charge localization [23]. However, the original locations of protons are not strictly determined experimentally because anthracene has ten hydrogen atoms, and their positions in a molecule are not equivalent with respect to the laser polarization plane.

In this study, we report the Coulomb explosion of multiply ionized linear molecules, α , ω -diiodoalkanes with one to six carbons in an alkyl chain. Contrary to the case with iodoalkanes [24-31], the ionization of diiodoalkanes [32, 33] and that of molecules with a long alkyl chain [34, 35] have not been well studied in intense femtosecond laser fields. The linear alkanes substituted with electron-rich iodine atoms are suitable substances to examine the charge localization (migration) because iodine is expected to hold positive charges [36]. The angular distributions of iodine and carbon ions were measured with respect to the laser polarization direction. The peak kinetic energies of carbon as well as of iodine ions increased as the number of carbons in an alkyl chain increased. These results are a strong indication that the energy gain mechanism is the Coulomb repulsion between the iodine ion and the adjacent carbon ions, not the Coulomb repulsion between the iodine ions. The charge localization before the Coulomb explosion in strong alternating electric fields is proposed.

2. Materials and methods

Diiodomethane (Aldrich, 99%), 1,3-diiodopropane (Aldrich, 99%), 1,4-diiodobutane (Aldrich, 99%), 1,5-diiodopentane (Tokyo Chemical Industry, >98.0%), and 1,6-

diiodohexane (Tokyo Chemical Industry, >98.0 %) were dried over diphosphorus pentoxide for few days. Those diiodoalkanes and 1,2-diiodoethane (Aldrich, 99%) were degassed by repeated freeze and thaw cycles before use. Xenon (Japan Air Gases, 99.99%) was used without further purification. The sample pressure in the ionization chamber was kept at 5.5×10^{-5} Pa during the experiments to avoid the space-charge effect.

The experimental details have been described elsewhere [37]. Briefly, the multiple ionization of diiodoalkanes and xenon was carried out with a 40-fs pulse centered at 0.8 μm (Thales laser, Alpha 100/1000/XS hybrid), and the ions were detected by a liner mode of Wiley-McLaren linear time-of-flight mass spectrometer (TOF-MS, Toyama, KNTOF-1800). 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 yield of ion emitted backward to the detector with large kinetic energy was limited due to a narrow slit located on the extraction plate. Thus, the ion emitted forward to the detector was used to evaluate ion yield and kinetic energy because whole ions were extracted and detected efficiently. The evaluation procedures of kinetic energy are described in elsewhere [38]. The direction of the laser polarization (linear) against the TOF axis was changed by a zero-order half-wave plate. The laser beam was

focused into the ionization chamber with a planoconvex quartz lens of 200 mm focusing length. The actual laser intensity of the linear polarized pulse at the focus was determined by measuring the saturation intensity, I_{sat} of xenon ($1.1 \times 10^{14} \text{ W cm}^{-2}$ for a 45 fs pulse) by the method of Hankin et al. [39], and the error in the determination of absolute laser intensity was about $\pm 10\%$. The ions of the diiodoalkanes were measured successively after the measurement of I_{sat} of xenon without, between two runs, changing experimental conditions.

Density functional theory calculations (Gaussian 09, B3LYP/ LanL2DZ) were performed to determine the equilibrium structures of diiodoalkanes [40].

3. Results and discussion

3.1. Ionization of diiodoalkanes in femtosecond laser fields.

Fig. 1 shows the time-of-flight mass spectra of three diiodoalkanes measured at around 10^{15} Wcm^{-2} . The prominent ions were atomic ions such as F^+ ($x = 1 - 4$) and H^+ . Though the ion intensity was small, $\text{C}^{\nu+}$ ($\nu = 1 - 3$), I^{5+} , and I^{6+} were produced from all diiodoalkanes. In addition, the mass spectra contained singly and doubly charged intact molecular ions (M^+ , M^{2+}), an iodine-loss ion ($[\text{M}-\text{I}]^+$), and a series of hydrocarbon fragment ions such as C_nH_m^+ . The Keldysh adiabaticity parameter γ is the index that

defines the border between the multiphoton ionization and the tunnel ionization regimes of atoms, and γ is derived by the ionization potential and ponderomotive potential [41].

The tunnel ionization mechanism dominates when γ is smaller than unity. The first vertical ionization potentials of diiodomethane, diiodoethane, diiodopropane, diiodobutane, and diiodohexane were 9.46 [42], 9.50 [43], 9.37 [44], 9.32 [44], and 9.28 eV [44], respectively. The γ of those diiodoalkanes at $1.0 \times 10^{15} \text{ Wcm}^{-2}$ ($0.8 \mu\text{m}$) was calculated to be ca. 0.28. Thus, it is safe to say that the laser intensity used in this study is within the field ionization regime for singly charged molecular ion formation.

Moreover, the observation of multiply charged atomic ions such as I^{6+} indicates that further ionization by sequential tunneling processes occurs at this laser intensity. As a result of the strong Coulomb repulsion in MMCs, atomic ions fly away with a certain kinetic energy. The split peaks found in all atomic ions are a typical feature of an ion generated by Coulomb explosion [2]. Since ions with certain kinetic energies are emitted along the forward or backward directions relative to the ion flight axis in TOF-MS, these respective ions are detected at earlier or later times in the TOF spectrum, hence at a smaller or larger mass-to-charge ratio (m/z) in a mass spectrum.

It should be mentioned that the origin of multiply charged atomic ions is different from that of molecular ions or that of fragment ions. Due to the spatial and temporal

distribution of laser intensity, high charge states that form atomic ions are formed at the most intense part of the laser pulse in both space and time, whereas molecular ions and fragment ions are formed at the wing of the laser beam (in space) as well as at the leading and trailing edges of the laser pulse (in time) where the laser intensity is low. Therefore, we will not discuss the molecular ions and fragment ions because they are not within the scope of this study.

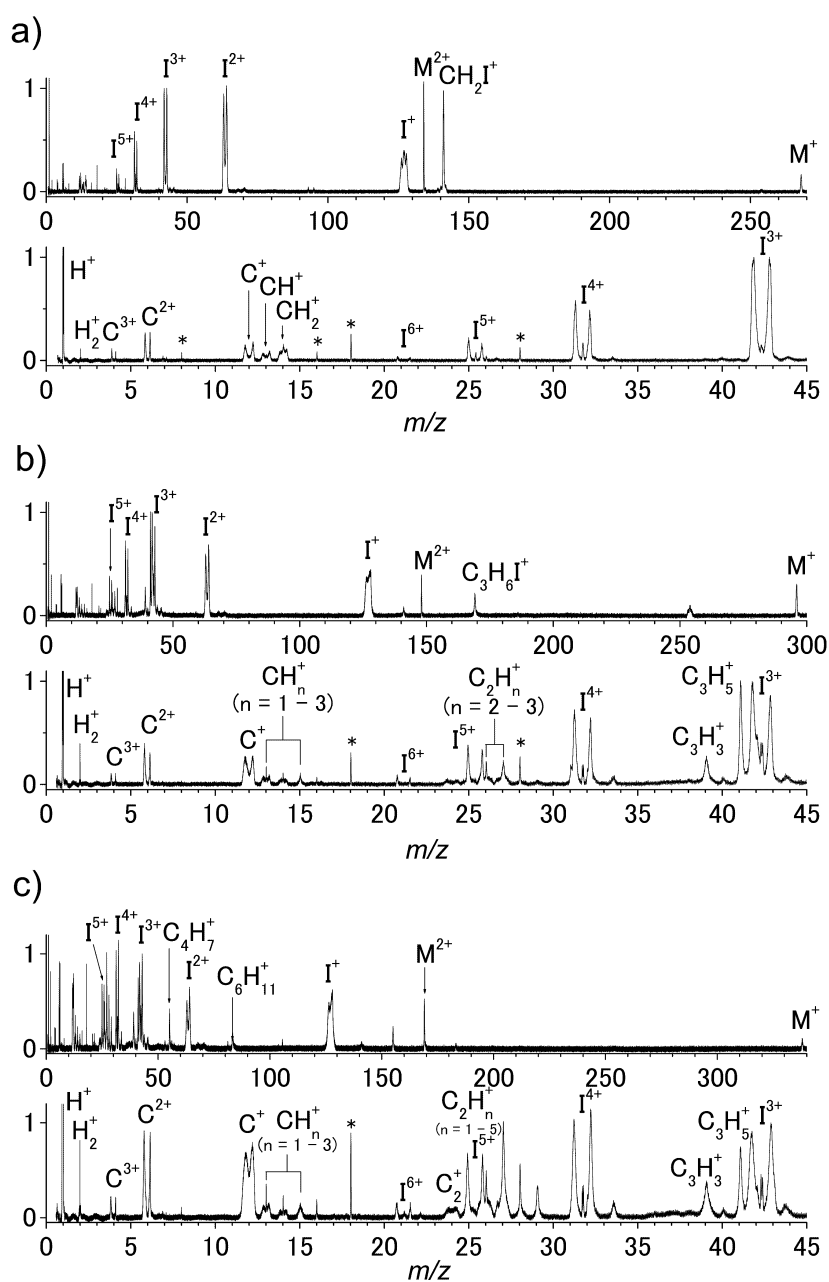


Fig. 1. Mass spectra of (a) diiodomethane at $4.7 \times 10^{15} \text{ Wcm}^{-2}$, (b) 1,3-diiodopropane at $3.5 \times 10^{15} \text{ Wcm}^{-2}$, (c) 1,6-diiodohexane at $3.8 \times 10^{15} \text{ Wcm}^{-2}$. The laser polarization direction was parallel to the ion flight axis. The asterisks indicate impurities originating from contaminated water, nitrogen, and oxygen.

3.2. Anisotropic emission of atomic ions.

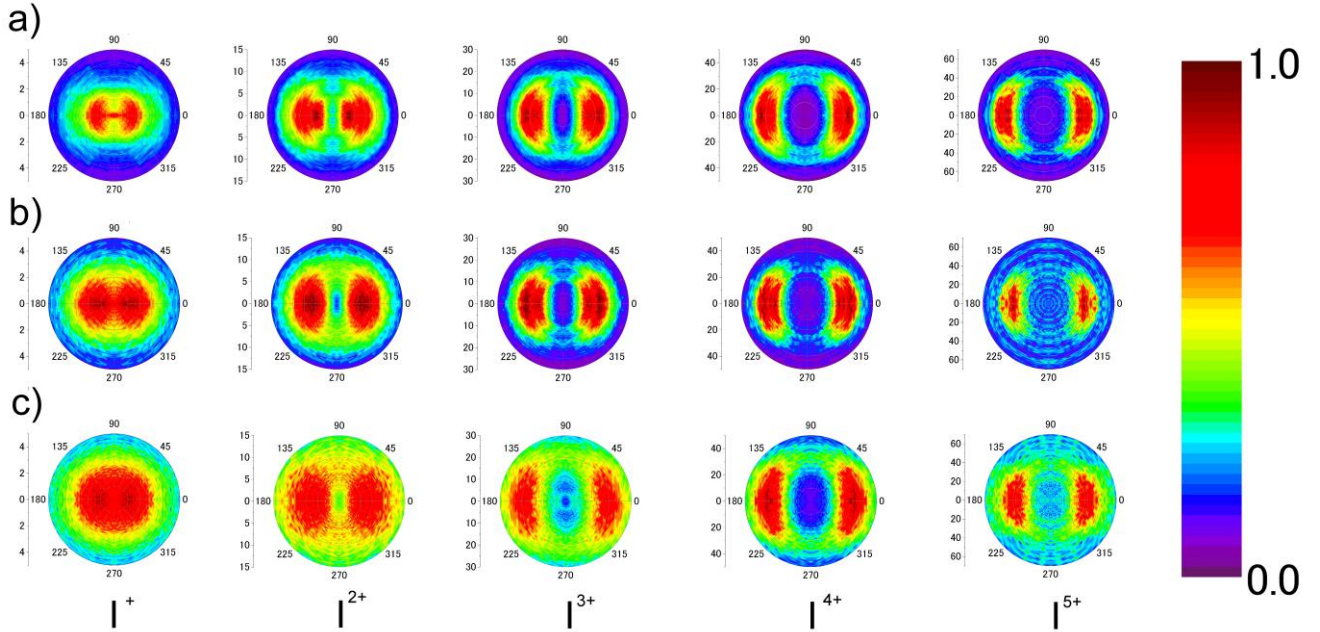


Fig. 2. Angular distributions of I^{x+} ($x = 1 - 5$) ejected from a) diiodomethane at 1.7×10^{15} Wcm^{-2} , b) 1,3-diiodopropane at 1.9×10^{15} Wcm^{-2} , and c) 1,6-diiodohexane at 1.4×10^{15} Wcm^{-2} in polar coordinates. The angles are the relative angles with regard to the polarization plane of the laser fields from the ion flight axis to the detector. The radius stands for the kinetic energy in eV units. The ion intensity normalized to unity at peak ion intensity in the polar plot is expressed by a linear color code.

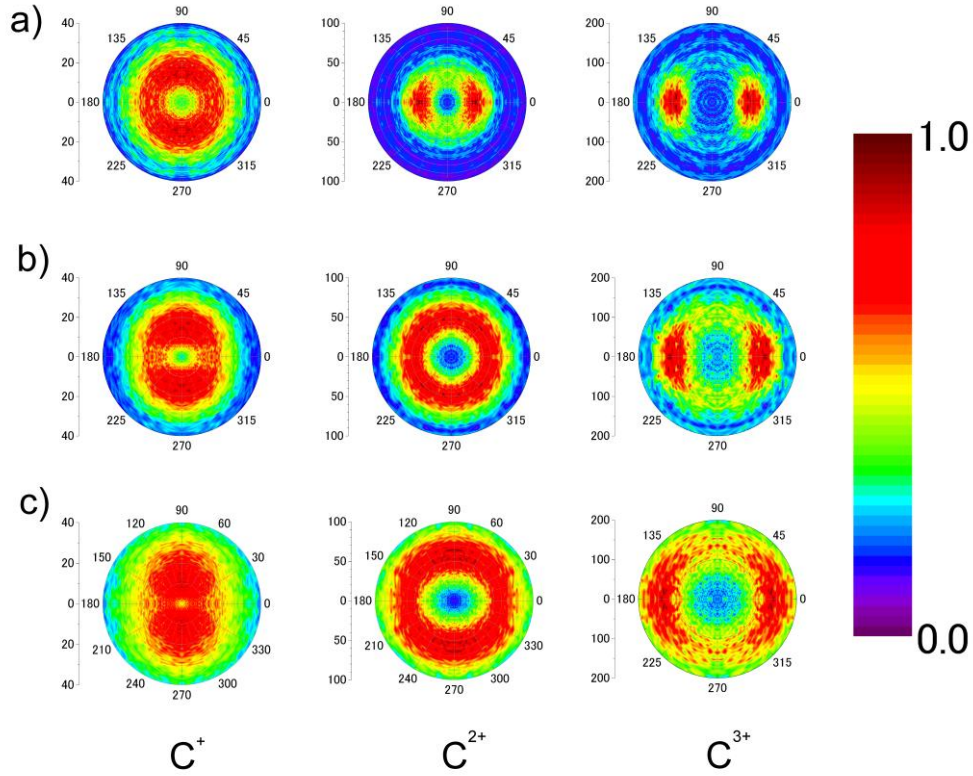


Fig. 3. Angular distributions of C^{y+} ($y = 1 - 3$) ejected from a) diiodomethane at $1.7 \times 10^{15} \text{ Wcm}^{-2}$ (C^{3+} , $3.6 \times 10^{15} \text{ Wcm}^{-2}$), b) 1,3-diiodopropane at $1.9 \times 10^{15} \text{ Wcm}^{-2}$ (C^{3+} , $7.1 \times 10^{15} \text{ Wcm}^{-2}$), and c) 1,6-diiodohexane at $1.4 \times 10^{15} \text{ Wcm}^{-2}$ (C^{3+} , $3.7 \times 10^{15} \text{ Wcm}^{-2}$) in polar coordinates. The angles are the relative angles with regard to the polarization plane of the laser fields from the ion flight axis to the detector. The radius stands for the kinetic energy in eV units. The ion intensity normalized to unity at peak ion intensity in the polar plot is expressed by a linear color code.

Figs. 2 and 3 compare the angular distribution of I^{x+} ($x = 1 - 5$) and C^{y+} ($y = 1 - 3$) in polar coordinates for three diiodoalkanes. Those of C^{3+} were measured at relatively high laser intensity to achieve a good signal-to-noise ratio (S/N). Here we define the angle that was measured with respect to the polarization plane of the laser fields from the ion flight axis to the detector: parallel (0, 180 degrees), orthogonal (90, 270 degrees). The data were measured for the two quadrants with 4-degree steps experimentally, and then averaged to improve the S/N because the quadrants were almost identical. Finally, the averaged data were used to make a polar plot for clearer presentation.

The anisotropic angular distributions with respect to the laser polarization direction were observed for most of the iodine and carbon ions. The origin of anisotropy in the ion angular distribution is the geometric selection in the tunnel ionization process, although the molecules are randomly oriented in the gas phase. Assuming that a linearly polarized laser pulse is used for ionization, the probability of tunnel ionization of molecules depends on how they are aligned with respect to the polarization direction of the laser pulse [45]. Because the ensuing multiple ionization processes will be regulated by the initial ionization step, anisotropic emission of ions from MMCs with respect to the laser polarization direction is observed [46].

As shown in Fig. 2, the anisotropic emissions of the iodine ions located on either edge of the alkyl chain indicate that diiodoalkanes aligned along the laser polarization direction were highly ionized. This trend is similar to that of linear rigid molecules such as diiodoacetylene (DIA, I-C \equiv C-I) [47] and diiododiacetylene (I-C \equiv C-C \equiv C-I) [37]. As the charge number increased, the emission of iodine ion showed a sharp distribution along the laser polarization direction. This feature was more prominent for diiodohexane than for diiodomethane. Here we define the extinction ratio, i.e., the ratio of the ion intensity (peak value) measured under an orthogonal condition to that measured under a parallel condition, for a quantitative discussion of anisotropic ion emissions. Fig. 4 shows the extinction ratios of iodine ions as functions of the number of carbons in an alkyl chain and the charge number of iodine ions. The extinction ratios of iodine ions were 0.26–0.48 (diiodomethane), 0.16–0.42 (diiodoethane), 0.33–1.0 (diiodopropane), 0.26–0.83 (diiodobutane), 0.21–0.91 (diiodopentane), and 0.40–0.90 (diiodohexane). We previously reported that the extinction ratios of proton and carbon ions ejected from acetylene at $1.2 \times 10^{15} \text{ Wcm}^{-2}$ are equal to zero [47]. It was noteworthy that the extinction ratios of iodine ions were more than 0.2, although iodine atoms in diiodoalkanes were located on both edges of the molecules. The dotted lines in Fig. 4 indicate the trends in the change of extinction ratios against the charge number.

For the cases of diiodomethane and diiodoethane, all the extinction ratios except for that for I^+ were independent of the charge number. On the other hand, the extinction ratios increased as the charge number decreased when there were more than three carbons in an alkyl chain. In addition, the extinction ratios of I^+ , I^{2+} , and I^{3+} suddenly became large when there were more than three carbons.

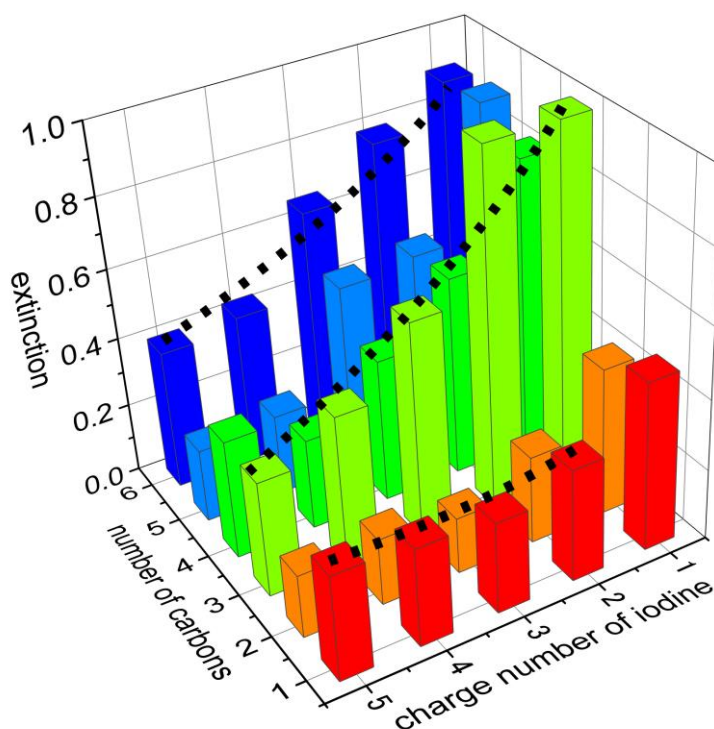


Fig. 4. Extinction ratios of iodine ions as a function of the number of carbons in an alkyl chain or the charge number of iodine. Dotted lines for diiodomethane, diiodopropane, and diiodohexane are drawn to guide the eye.

The angular distributions of carbon ions depended strongly on the charge number, as shown in Fig. 3. The angular distribution of C^+ showed an elliptic distribution with a long axis orthogonal to the laser polarization direction. C^{2+} was ejected in an isotropic manner except in the cases of diiodomethane and diiodoethane (not shown). In all diiodoalkanes, C^{3+} was ejected mostly in a parallel direction, but the extinction ratio depended strongly on the number of carbons in an alkyl chain. In the case of diiodomethane, C^{3+} was emitted in a parallel direction (extinction ratio: 0.09). In contrast, the emission of C^{3+} in an orthogonal direction became pronounced in the case of diiodopropane (extinction ratio: 0.65). The angular distribution of C^{3+} from diiodohexane was broad and nearly isotropic (extinction ratio: 0.84).

Here we consider the emission behavior of iodine and carbon ions from the view point of alignment in strong laser fields. Iodine atoms are substituted on both edges of an alkyl chain. Therefore, in principle the extinction ratios should be much less than unity if the perfect alignment is achieved because the emission of iodine ions is not obstructed by other atoms at all. We have reported that the extinction ratios of iodine ions ejected from DIA at $3.6 \times 10^{14} \text{ Wcm}^{-2}$ are 0.63 (I^+), 0.27 (I^{2+}), 0.08 (I^{3+}), 0.01 (I^{4+}), and 0 (I^{5+}) [47]. It is noted that those extinction ratios become large at $1.2 \times 10^{15} \text{ Wcm}^{-2}$: 0.61 (I^+), 0.36 (I^{2+}),

0.23 (I^{3+}), 0.14 (I^{4+}), 0.04 (I^{5+}). The increase in the extinction ratios of iodine ions is explained in terms of the saturation of the ionization rate at high laser intensity. In contrast, the minimum and maximum extinction ratios of iodine ions ejected from diiodoalkanes were 0.16 for I^{5+} and 1.0 for I^+ , respectively. These results are explained in terms of the imperfect alignment of diiodoalkanes. Generally, electrons will be stripped from the large-amplitude lobes of molecular orbitals along the laser polarization direction by tunneling if the ionization probability is not saturated [48, 49]. Ohmura et al. have shown that the molecules having the highest occupied molecular orbitals (HOMOs) with asymmetric structures are selectively ionized using asymmetric electric fields [50]. In their experiments, they have examined iodoalkanes such as iodomethane [29, 30] and 1-iodohexane [31]. Regardless of the number of carbons in an alkyl chain, the success of the selective ionization of oriented iodoalkanes reveals the importance of the geometric nature of a HOMO that is localized on an iodine atom. It should be noted that aligned rather than oriented multiply charged molecular cations would have been prepared by tunneling in the present study, because we used symmetric electric fields.

Fig. 5 shows the three highest molecular orbitals of three diiodoalkanes. It can be clearly seen that HOMO, HOMO-1, and HOMO-2 are localized on the iodine atoms. The contribution of electrons belonging to the low-lying molecular orbitals in an intense

laser ionization process has been investigated for some molecules [51-54]. It should be noted that highly charged states disappearing promptly to leave I^{6+} via the Coulomb explosion should be formed in our experiments. In principle, we need to consider further deeper-lying molecular orbitals to treat such states. However, consideration of such orbitals is beyond the scope of this study, and the highest occupied molecular orbital makes the most important contribution to ionization as the sequential multiple tunnel ionization processes will be regulated by the initial tunnel ionization step [46]. Therefore, we will consider only three highest molecular orbitals for qualitative discussions. If not only HOMO but also HOMO-1 and HOMO-2 were the origins of ionizing electrons, the electrons would be dominantly stripped from the iodine atoms located on both sides of the alkyl chain. Thus, it is expected that the contribution of the edge of a molecule in multiple ionization becomes dominant as the molecule grows longer. At the same time, the presence of carbons in the middle of the molecule in the multiple ionization process becomes less important as the molecule elongates, because those carbon atoms do not contribute to HOMO-1 and HOMO-2.

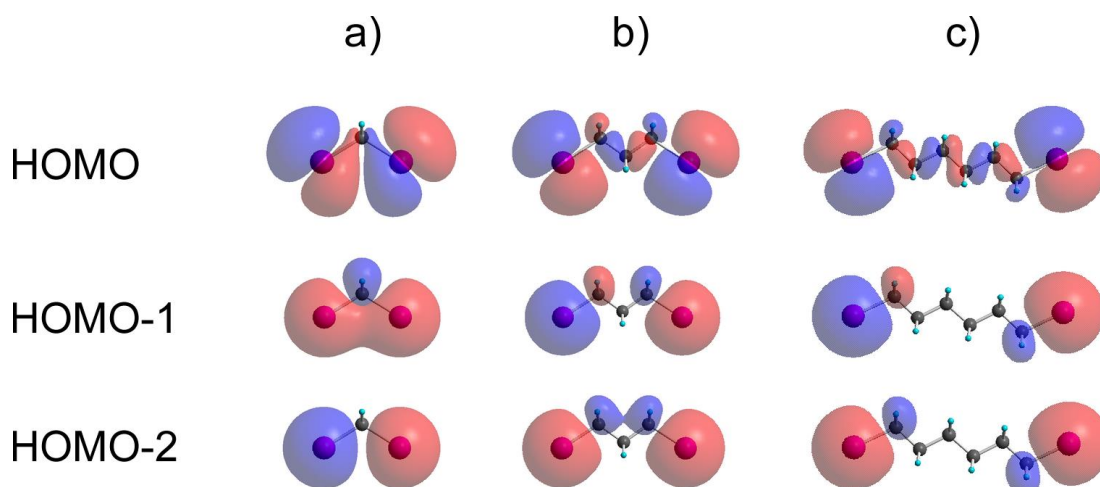


Fig. 5. The molecular orbitals of a) diiodomethane, b) 1,3-diiodopropane, and c) 1,6-diiodohexane calculated by using the Gaussian 09 software package (method: B3LYP; basis sets: LanL2DZ).

The largest lobes of HOMO are located on the iodine atoms of diiodoalkanes. Therefore, the selective ionization of aligned diiodoalkanes is expected as in the cases of iodoalkanes [29-31]. It should be noted that the iodine atoms of DIA are considered equivalent with respect to the laser polarization direction because the nodal planes of HOMO, HOMO-1, and HOMO-2 of DIA are parallel [36]. Therefore, selective ionization of aligned DIA is expected even though it has one iodine atom on each edge of the molecule. In contrast, the nodal planes of MOs are not parallel in the case of diiodoalkanes. Therefore, we should consider the electron emissions from MMCs of

different alignments with respect to the laser polarization direction by tunneling. An iodine ion is emitted by Coulomb explosion along the laser polarization direction, while another iodine ion is ejected along a line that is slightly inclined relative to the laser polarization direction after multiple ionizations. Consequently, the angular distribution of iodine ions ejected from diiodoalkanes becomes broad and the extinction ratios should not equal zero. Contrary to the case with DIA, the effect of alignment will not be strengthened even if both sides of the alkyl chain are substituted by iodine atoms because the relative configuration of the lobes on iodine atoms is independent due to C-C bond rotations. The above-mentioned considerations would be reasonable starting points for the interpretation of the observed angular distributions. However, more elaborated theoretical considerations including the contribution of lower-lying orbitals in addition to Dyson orbitals under various conditions are required for further discussions [55, 56].

Unlike the case with iodine atoms, we need to consider carbons of different locations in an alkyl chain and the heavy atom effect by iodine atoms in addition to imperfect alignment. A carbon atom is located between iodine atoms, between an iodine atom and a neighboring carbon atom, or between carbon atoms. Therefore, the emission of carbon ions is influenced by the terminal iodine atom(s) and/or neighboring carbon

atom(s). Furthermore, the angular distribution of carbon ions becomes broad as the number of carbon sites increases due to the nonlinear configuration of carbon atoms in diiodoalkanes. In the cases of diiodomethane and diiodoethane, the emission of C^{3+} showed strong anisotropy. This is presumably because the emission of carbon ions is dominated only by the neighboring iodine ions, i.e., carbon ions are expelled in the direction opposite that of iodine ions along with a C–I bond. In contrast, we need to consider the different locations of carbons for diiodoalkanes that have more than three carbons. For example, carbons in diiodopropane were ejected from two different sites, C_A and C_B (I- C_AH_2 - C_BH_2 - C_AH_2 -I). Similarly, diiodobutane, diiodopentane and diiodohexane have two, three, and three different carbon sites, respectively.

The terminal heavy atom effect has been found in a rigid linear molecule, DIA, from which C^+ and C^{2+} were mostly emitted in an orthogonal direction. This phenomenon was attributed to heavy iodine ion obstacles disturbing the direction of movement of the light carbon ions, while the structural deformation enabled them to fly away in an orthogonal direction [47]. We have reported the extinction ratios of carbon ions ejected from DIA at $3.6 \times 10^{14} \text{ Wcm}^{-2}$ are 1.4 (C^+), 6.8 (C^{2+}), and 15 (C^{3+}), respectively [47]. These values decrease at $1.2 \times 10^{15} \text{ Wcm}^{-2}$: C^+ , 1.2; C^{2+} , 1.5; C^{3+} , 1.5 [47]. It should be mentioned that the extinction ratios of carbon ions ejected from diiododiacetylene are

larger than those of carbon ions ejected from DIA, i.e., the ejections of carbon ions in an orthogonal direction with respect to the laser polarization direction are enhanced in longer acetylene derivatives [37]. The large extinction ratios are attributed to one or more of the following: the close proximity of iodine to the carbons even at highly charged states, a higher degree of carbon ion emission blocking, and a higher degree of deformation of the molecular skeleton in bending coordinates. On the other hand, the extinction ratios of C^+ , C^{2+} , and C^{3+} ejected from diiodoalkanes were 1.2, 0.41, and 0.09 (diiodomethane), 1.0, 0.71, and 0.65 (diiodopropane), and 1.1, 1.0, and 0.84 (diiodohexane), respectively. We conclude that the different trends in the extinction ratios of carbon ions against the length of molecules between the iodine-substituted acetylenes and alkanes originate in the differences in geometric selection, rigidity, linearity, and deformation coordinates. The heavy atom effect is not significant in the cases of diiodoalkanes, probably because the deformation of the molecular skeleton is not important in light of the nonrigid and nonlinear structures of diiodoalkanes. Moreover, the deformation of the molecular skeleton consisting of C–C single bonds in stretching coordinates rather than in bending coordinates is expected in the cases of iodine-substituted alkanes.

3.3. Kinetic energy increases in longer diiodoalkanes.

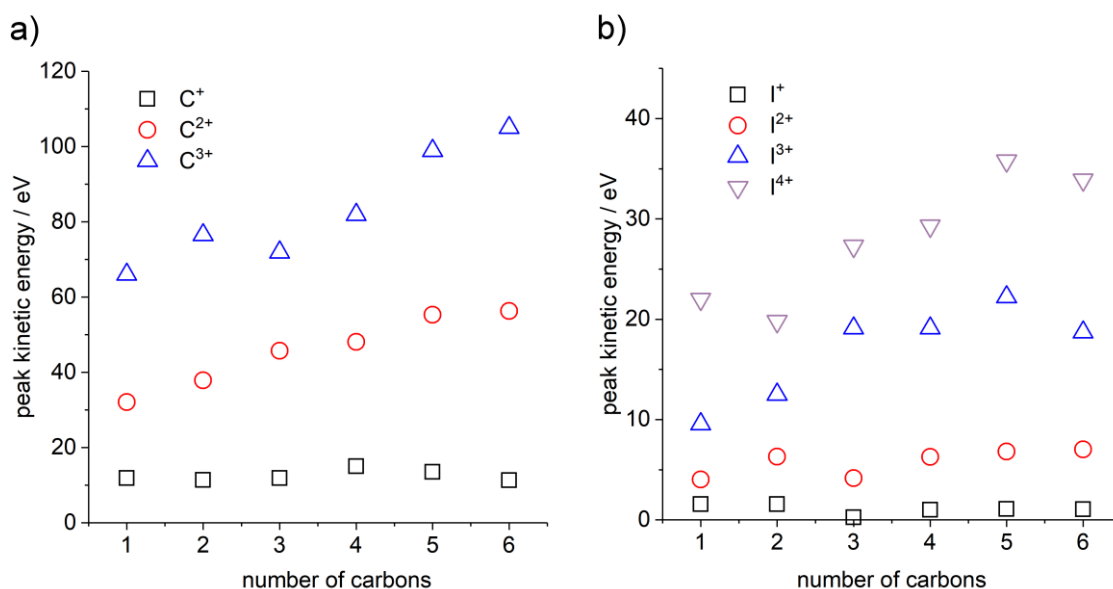


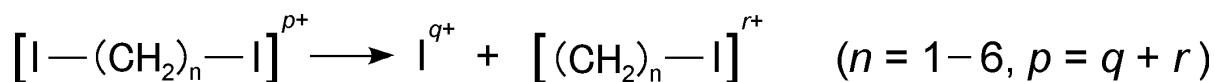
Fig. 6. The peak kinetic energy of (a) carbon (C⁺, squares; C²⁺, circles; C³⁺, triangles) and (b) iodine ions (I⁺, squares; I²⁺, circles; I³⁺, triangles; I⁴⁺, inverted triangles) ejected from diiodoalkanes as a function of the number of carbons in an alkyl chain.

The peak kinetic energies of iodine and carbon ions as a function of the number of carbons in an alkyl chain are shown in Fig. 6. The kinetic energies of I⁵⁺ and I⁶⁺ were not obtained because their ion peaks were small and/or overlapped with other fragment ion peaks. For the cases of I⁺, I²⁺, and C⁺, the kinetic energies were almost independent of the number of carbons in an alkyl chain. In contrast, the kinetic energies of highly charged atoms

were monotonically increased (C^{2+} , 175%; C^{3+} , 159%; I^{3+} , 196%; I^{4+} , 154%) as the number of carbons in an alkyl chain increased from one to six. It is noted that the kinetic energies of I^{3+} and I^{4+} seem to be saturated when there are more than five carbons. We need to consider the origin of the dependence of kinetic energy variations on the number of carbons in an alkyl chain. The kinetic energies of carbon ions ejected from diiodoalkanes were much higher than those of acetylene but similar to those of DIA [47]. We have reported that the kinetic energies of ions ejected from DIA at $1.2 \times 10^{15} \text{ Wcm}^{-2}$ are 14 (C^+), 58 (C^{2+}), 130 (C^{3+}), 1.4 (I^+), 6.2 (I^{2+}), 16 (I^{3+}), and 30 eV (I^{4+}) [47]. It is emphasized that the kinetic energy of ions ejected from diiodoalkanes became closer to that of ions ejected from DIA as the alkyl chain became longer. The comparison of kinetic energy between diiodoalkanes and DIA is quite informative because the interaction between terminal iodine atoms and neighboring carbons is more significant in longer diiodoalkanes, although the distance between terminal iodine atoms is long. The distance between the terminal iodine atoms in neutral diiodoalkanes varies from 2.8 (diiodomethane) to 9.8 Å (diiodohexane). Therefore, the kinetic energy of iodine ions should decrease as the molecule becomes longer if the Coulomb repulsion of the iodine ion is dominated by the other iodine ion. However, this expectation contradicts our experimental observations: The kinetic energy of an iodine ion increased as the number

of carbons in an alkyl chain increased. Therefore, we can conclude that the kinetic energy of iodine is not determined by the other iodine ion but by neighboring carbon ions. In addition, only one iodine atom may be highly charged at the instant of a Coulomb explosion.

The longer diiodoalkanes result in higher kinetic energies of iodine and carbon ions. We could consider momentum conservation and charge localization to explain this trend. Supposing that the two-body Coulomb explosion occurs in diiodoalkanes, the kinetic energy of iodine ions is determined by the charge numbers and the distance between two ions. The most probable dissociation process would be the C–I bond cleavage as mostly found in electron impact ionization (Scheme 1).



Scheme 1. Proposed initial two-body Coulomb explosion process of diiodoalkanes.

If this two-body Coulomb explosion occurs, the kinetic energy of iodine ions depends on the length of the C–I bond at the instant of the Coulomb explosion. Noted that we must consider the elongation of the C–I bond during the laser pulse [57, 58]. However, the trend of kinetic energy variations of iodine ions found in this study would not be related to the difference of bond elongation since we can expect that the degree of elongation of

the C–I bond is similar for all diiodoalkanes. Another factor should determine the kinetic energy of iodine ions; however, the two-body Coulomb explosion process shown in Scheme 1 should be dominant due to the following reasons. Due to the momentum conservation law, a light fragment ion carries high kinetic energy, whereas a heavy counter-ion is expelled with low kinetic energy in the Coulomb explosion process. Therefore, we need to consider the Coulomb explosion of diiodoalkanes occurring between an iodine ion and the counterpart fragment ion involving an iodine atom. If Coulomb explosion occurred via multi-body manner and/or C–C bond cleavage, the kinetic energy of an iodine ion would be much lower than the peak kinetic energy observed in this study. The nominal masses of diiodoalkanes vary from 268 (diiodomethane) to 338 (diiodohexane). Therefore, the ratio of the kinetic energy gained by an iodine ion varies from 0.53 ($=141/268$, diiodomethane) to 0.62 ($=211/338$, diiodohexane) if the above-mentioned two-body Coulomb explosion takes place. Consequently, the kinetic energy of iodine ions ejected from diiodohexane is expected to be 117% ($=0.62/0.53$) higher than that of iodine ions ejected from diiodomethane if the above-mentioned hypothesis is correct. However, this value is smaller than that obtained in the experiments (~196%). Therefore, another effect that increases kinetic energy of iodine ions when the length of an alkyl chain becomes longer should be considered.

Another possible explanation of the kinetic energy variations depending on the length of the alkyl chain is the charge localization on the edge of a molecule before the Coulomb explosion. Fig. 5 shows that the electrons belonging to the three highest MOs are absent on the carbon atoms in the middles of diiodoalkanes having longer alkyl chains. Therefore, it is expected that only the edge of the molecule becomes electron-deficient at the initial stage of ionization. Rapid charge delocalization is expected to occur even if electrons are stripped from the edge of the molecule. However, the charge migration after removing the electrons belonging to lower-lying orbitals is expected to be slower than that after removing the electrons in HOMO [19]. It should be mentioned that we have shown that the tetracation of diiodoacetylene remains metastable towards dissociation because of the localization (>90%) of the positive charges on the terminal iodine atoms [36]. The nonequilibrium distribution of electrons (positive charges) in diiodoalkanes could be easily attained during ionization in intense alternative electric fields because the terminal iodine atoms can trap positive charges. We could propose that the Coulomb repulsion between the terminal iodine and neighboring carbons is enhanced when the length of an alkyl chain becomes longer. Time evolution of charge [19] and the control of charge migration [18] within the framework of cation radical

have been reported. However, those of MMCs are still theoretical and experimental challenges. We hope that the investigation of the time evolution of positive charges in a MMC and the charge density of MMC at the instant of a Coulomb explosion by using elaborated theories would clarify the effect of molecular length on the kinetic energy of iodine ions.

4. Conclusion

We have determined that the length of α , ω -diiodoalkanes is an important factor in determining the angular distribution and kinetic energy of ions formed by a Coulomb explosion in intense femtosecond laser fields. In contrast to rigid linear diiodoacetylene, the influences of the terminal heavy iodine atoms on the blocking of carbon ion emission, and of the deformation of the molecular skeleton in bending coordinates, are not significant due to the nonrigidity and bended carbon chain structure of diiodoalkanes. The selective ionization of molecules is attained in part because the molecular orbitals localized on the edges of molecules are independent due to the free rotation of the C–C bonds. The kinetic energies of iodine and carbon ions increase as the alkyl chain becomes longer. The enhancement of charge localization that results in the stronger Coulomb repulsion between the terminal iodine and neighboring carbons should be taken into

accounts to explain the effect of molecular length on the kinetic energy of ions. The rigid molecules involving marker atoms such as those of iodine and tunable spacer/linkage modules are promising candidates for further investigation of the charge localization effect in the Coulomb explosion process [37]. Moreover, nonadiabatic alignment by using longer-duration laser pulses before ionization by femtosecond intense laser pulses is very helpful for regulating the ion emissions from linear molecules.

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