

## 論文内容の要旨

# Decomposition of trapped cyclohexane ions in intense laser fields and development of an ion beam apparatus

(強光子場中のシクロヘキサニイオンの分解反応及びイオンビーム装置の開発)

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### 1. Introduction

When molecules interact with ultrashort intense laser pulses, they are ionized immediately at the leading edge of the temporal envelope of the laser pulses. Consequently, in most cases, characteristic molecular dynamics in intense laser fields, such as deformation of the geometrical structure of molecules, chemical-bond rearrangement, decomposition, and Coulomb explosion, proceed in their ionic states. Therefore, investigation of molecular dissociation dynamics starting from molecular ion species having the specific mass and charge will give us essential information on the mechanism of molecular dynamics in intense laser fields. However, such experiments are difficult in general because the sample density of molecular ions is inevitably extremely low around  $10^7 \text{ cm}^{-3}$  or lower under typical experimental conditions. Consequently, the number of experimental reports on dissociation processes of molecular ions in intense laser fields is much fewer than those of experiments starting from neutral molecules. In the previous studies of photodissociation processes of molecular ions, the molecular ions were mostly diatomic and triatomic molecular ions, as reviewed by Ben-Itzhak [1]. Indeed, intense-field photodissociation experiments for larger molecular ions containing more than three atoms have been reported only by two research groups, i.e., tandem time-of-flight type mass spectrometry on aromatic molecular ions by our group [2] and ion trap experiments on peptide ions by Reid's group [3]. In the present study, in order to investigate dissociation dynamics of mass-selected molecular ions in intense laser fields, I have investigated decomposition processes of cyclohexane molecular ion in intense laser fields by ion trap time-of-flight mass spectrometry, and have developed a mass-selective ion beam apparatus for coincidence measurements of fragment species generated through intense-field photodissociation of molecular ions.

### 2. Decomposition of cyclohexane ion in intense femtosecond laser fields by ion trap time-of-flight mass spectrometry

When neutral molecules are ionized by intense femtosecond laser pulses in the near-infrared region, decomposition into smaller sized fragment ion species is suppressed compared with picosecond and nanosecond laser ionization, and parent ions are observed as a main product ion. However, some molecular species like cyclohexane exhibit significant fragmentation even when they are ionized with near-infrared femtosecond pulses. Nakashima and coworkers [4] suggested that such fragmentation proceeds when singly charged parent ions have a one-photon absorption band at the wavelength of the ionization laser pulses. In the present study, in order to clarify the mechanisms through which parent

ion species are decomposed into fragments, we have investigated the laser-field intensity dependence of the decomposition processes of cyclohexane cations stored in the ion trap by irradiating them with intense femtosecond laser pulses at 800 nm at the different laser field intensities ( $I$ ) in the wide range of  $5.7 \times 10^{11} \sim 8.0 \times 10^{13} \text{ W/cm}^2$ .

Figure 1 shows the schematic of the experimental setup. The apparatus is composed of a molecular beam source, a Paul-type ion trap, and a time-of-flight (TOF) mass spectrometer. Neutral cyclohexane molecules were introduced as an effusive molecular beam into the central area of the ion trap mounted in a vacuum chamber, and were ionized by femtosecond laser pulses. The generated cyclohexane parent ions were trapped exclusively by adjusting radiofrequency voltages applied to ion-trap electrodes. By repeating the ion generation and the mass-selective trapping around 150 times, cyclohexane ion ( $\text{C}_6\text{H}_{12}^+$ ;  $m/z = 84$ ) were accumulated in the ion trap. The stored  $\text{C}_6\text{H}_{12}^+$  ions were irradiated with an intense femtosecond laser pulse in the wide intensity range of  $5.7 \times 10^{11} \sim 8.0 \times 10^{13} \text{ W/cm}^2$ , and were decomposed into smaller fragment species. The generated fragment ions were extracted from the ion trap by applying pulsed high-voltage to the end-cap electrodes of the ion trap, and were recorded by TOF mass spectrometry. Because signals of the fragment ions were extremely weak, TOF data recorded at each laser-shot were transferred into a personal computer and analyzed by the ion counting scheme to raise the signal-to-noise ratio of the mass-spectra. In order to suppress ion signals originating from the dissociative photoionization of background neutral  $\text{C}_6\text{H}_{12}$ , the electrodes of the ion trap were cooled down to  $\sim 77 \text{ K}$  with liquid nitrogen for reduction of the number density of neutral  $\text{C}_6\text{H}_{12}$  by the cryogenic-pump effect and the background pressure of the vacuum chamber was kept to be about  $3 \times 10^{-7} \text{ Pa}$ .

In order to investigate decomposition process from  $\text{C}_6\text{H}_{12}^+$ , only the  $\text{C}_6\text{H}_{12}^+$  species must be stored before the irradiation of the laser pulse that induces decomposition. The TOF mass spectrum in Fig. 2 shows that the mass-selective accumulation of  $\text{C}_6\text{H}_{12}^+$  was achieved successfully before the irradiation of a laser pulse inducing the decomposition.

Figure 3(a) shows a mass spectrum of the fragment ions generated through the photodecomposition of the stored  $\text{C}_6\text{H}_{12}^+$  obtained by the irradiation of a femtosecond laser pulse at the field intensity of  $8.0 \times 10^{13} \text{ W/cm}^2$ . Various kinds of ion species, such as  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_n^+$  ( $n = 2\sim 6$ ),  $\text{C}_3\text{H}_n^+$  ( $n = 3\sim 7$ ),  $\text{C}_4\text{H}_n^+$  ( $n = 5\sim 8$ ), and  $\text{C}_5\text{H}_n^+$  ( $n = 7, 9$ ), were observed as the product fragment ions. Figure 3(b) shows a mass spectrum of fragment ions when the laser field intensity was  $5.7 \times 10^{11} \text{ W/cm}^2$ . At this weaker intensity, the signal intensities of small fragment ions decreased drastically relative to the signal intensity of Fig. 3(a), suggesting that absorption of a larger number of photons is necessary for generating the small fragment ions.

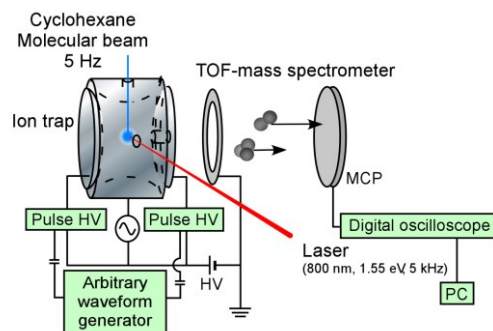


Fig. 1. Schematic of an ion trap time-of-flight mass spectrometry apparatus.

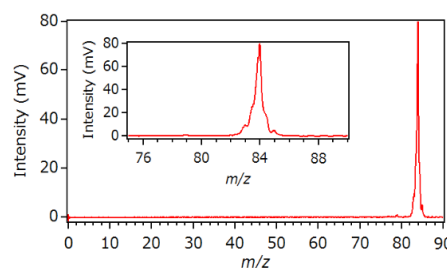


Fig. 2. Mass spectrum of the trapped ions after the mass-selective ion accumulation for cyclohexane parent ions. Inset: The expanded view around the peak of  $\text{C}_6\text{H}_{12}^+$ .

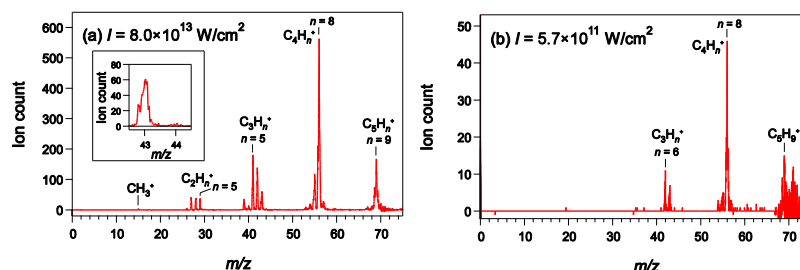


Fig. 3. Mass spectra of the fragment ions generated through the photodissociation of the stored  $\text{C}_6\text{H}_{12}^+$  obtained by the irradiation of femtosecond laser pulses: (a)  $I = 8.0 \times 10^{13} \text{ W/cm}^2$ . (b)  $I = 5.7 \times 10^{11} \text{ W/cm}^2$ .

Figure 4 shows a double logarithmic plot of the yields of fragment ion species generated from  $C_6H_{12}^+$  as a function of the laser field intensity. The straight lines in the plot show the results of the least-square fitting. Because the slopes for fragment ions, such as  $C_5H_9^+$ ,  $C_4H_8^+$ , and  $C_3H_6^+$ , were around 1.0 or smaller than 1.0, these fragment ions can be regarded as those generated through one-photon absorption. On the other hand, the ion yield of  $C_3H_5^+$  exhibits a sharp increase when  $I$  increases from  $I = 2.8 \times 10^{12}$  W/cm<sup>2</sup> to  $1.7 \times 10^{13}$  W/cm<sup>2</sup>, resulting in the slope of 2.21(9), implying that  $C_3H_5^+$  is generated through multiphoton absorption. However, when  $I > 1.7 \times 10^{13}$  W/cm<sup>2</sup>, the ion yields of  $C_3H_5^+$  are fitted well by a straight line with the slope of 1.11(3), which indicates that the yield of  $C_3H_5^+$  is suppressed by the resonant absorption of another photon for a strong electronic resonance between an electronically excited state of  $C_6H_{12}^+$  yielding fragmentation into  $C_3H_5^+$  and a higher electronic state yielding smaller fragment species. From the similar considerations based on the laser-field intensity dependences of the yields of 13 kinds of fragment ion species, it has been estimated that (i)  $C_5H_9^+$ ,  $C_4H_n^+$  ( $n = 6\sim 8$ ), and  $C_3H_n^+$  ( $n = 6, 7$ ) are produced from  $C_6H_{12}^+$  via one-photon absorption, (ii)  $C_4H_5^+$ ,  $C_3H_n^+$  ( $n = 4, 5$ ), and  $C_2H_4^+$  are produced via two-photon absorption, and (iii)  $C_3H_3^+$  and  $C_2H_n^+$  ( $n = 3\sim 5$ ) are produced via three photon absorption.

### 3. Development of a mass-selective ion beam apparatus for investigation of dissociation dynamics of molecular ions in intense laser fields

Dynamics of molecules in intense laser fields has been elucidated in detail by the analyses of 3D momenta of fragment ions recorded by coincidence momentum imaging (CMI) technique [5]. Ben-Itzhak [1] and coworkers combined CMI with a mass-selective molecular ion beam source equipped with a magnetic-sector mass filter, and performed complete analyses of 3D momenta of all the fragment species including neutral fragments generated from small molecular ions, such as  $H_2^+$ ,  $N_2^+$ , and  $O_2^+$ . For investigating dissociation dynamics of more complex molecular ions such as hydrocarbon molecular ions in intense laser fields, we developed a mass-selective ion beam apparatus equipped with an ion beam source and a quadrupole mass-filter whose mass-resolution is  $m/\Delta m \sim 48$ .

The mass-selective ion beam apparatus is composed of a duoplasmatron ion source, a quadrupole mass filter, a quadrupole deflector, a set of twelve disk electrodes, and a time-and-position sensitive detector, as shown in Fig. 5. An ion beam generated by the ion source is introduced into the mass filter, and the resultant mass-selected ion beam is deflected at right angles by the deflector, and introduced into the set of disk electrodes, where the ion beam is decelerated before interacting with an intense laser field, and then, the fragment ions are reaccelerated, so that the ionic fragments are mass-analyzed and discriminated from neutral fragments. From the arrival times of fragment species and their positions at the detector, momenta of all the fragment species are obtained.

In order to examine the performance of the ion beam apparatus, a mass-selected  $CO_2^+$  ion beam was generated. The ion beam current of  $CO_2^+$  was about 300 pA at the kinetic energy of 3 keV. The ion beam profile recorded by a MCP equipped with a phosphor screen was an ellipse whose lengths of major and minor axes were 2.1 mm and 1.7 mm in FWHM, respectively. From the beam profile and the beam current, the ion density was estimated to be  $\sim 6 \times 10^3$  cm<sup>-3</sup>. The ion beam is irradiated with femtosecond laser pulses with the diameter of 100  $\mu$ m at the repetition rate of 5 kHz. By

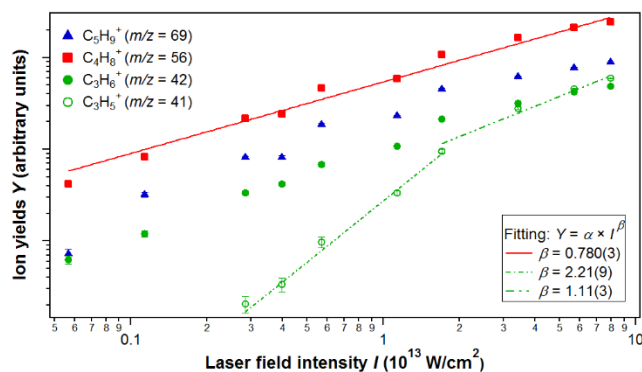


Fig. 4. Laser-field intensity dependences of the yields of the fragment ions produced by the irradiation of femtosecond intense laser pulses onto  $C_6H_{12}^+$ .

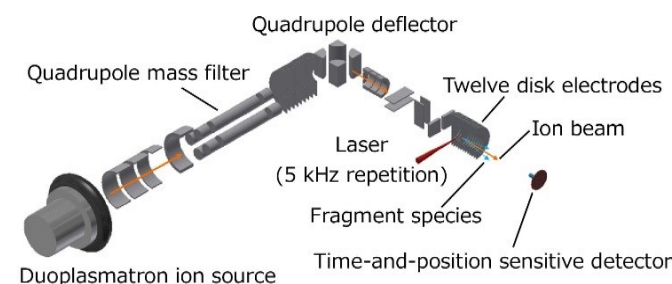


Fig. 5. Schematic of the mass-selective ion beam apparatus.

assuming that 1% of the  $\text{CO}_2^+$  ions in the interaction region dissociate into fragments, the signal count rate was estimated to be  $\sim 2$  counts per second, which is sufficiently large for coincidence measurements.

#### 4. Conclusion

By the ion-trap mass spectrometry, decomposition processes of cyclohexane cation  $\text{C}_6\text{H}_{12}^+$  induced by the irradiation of an femtosecond intense laser pulse were investigated. From the laser-field intensity dependences of the yields of the fragment ions produced from  $\text{C}_6\text{H}_{12}^+$ , the numbers of photons absorbed by  $\text{C}_6\text{H}_{12}^+$  were estimated for respective fragmentation channels, and the photodecomposition pathways were identified. The efficient fragmentation processes induced when neutral  $\text{C}_6\text{H}_{12}$  is irradiated with an intense laser pulse was ascribed to the resonant one-photon absorption and additional absorption of one or two photons in the  $\text{C}_6\text{H}_{12}^+$  cation stage. Furthermore, we developed the mass-selective ion beam apparatus, and its performance has been examined. From the profile and the current of mass-selected  $\text{CO}_2^+$  ion beam, it was confirmed that the  $\text{CO}_2^+$  ion density generated by the present ion beam apparatus is sufficiently large for coincidence measurements.

#### References

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