Decomposition of Cyclohexane Ion Induced by Intense Femtosecond Laser Fields

Takao Yamazaki, Reika Kanya, Kaoru Yamanouchi
Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
tyamazaki@chem.s.u-tokyo.ac.jp

Abstract: Decomposition of cyclohexane cations induced by an intense femtosecond laser field was investigated by ion trap time-of-flight mass-spectrometry. Laser intensity dependences of the yields of fragment ions revealed decomposition pathways producing the respective fragment ions.
OCIS codes: (020.0020) Atomic and molecular physics; (020.4180) Multiphoton processes

1. Introduction

When neutral molecules are ionized by intense femtosecond laser pulses in the near-infrared region, parent ions are produced as main product ions in most cases. However, some molecular species like cyclohexane exhibit significant fragmentation after the photoionization. Nakashima and coworkers [1] suggested that such fragmentation proceeds when singly charged parent ions have a one-photon absorption band at the wavelength of the ionization laser. In the present study, in order to clarify the mechanisms through which parent ion species are decomposed into fragments, we have investigated the intense-laser induced decomposition processes of mass- and charge-selected cyclohexane parent ions prepared in an ion trap based on the laser-field intensity dependences of the yields of the fragment ions.

2. Experimental

Figure 1 shows a schematic of the ion trap time-of-flight mass-spectrometry (TOF-MS) apparatus used in the present study. Neutral cyclohexane molecules were introduced as an effusive molecular beam into the central area of a Paul-type ion trap mounted in a vacuum chamber, and were ionized by femtosecond laser pulses (λ = 800 nm, $\Delta\tau$ = 40 fs, I = 6.3×10^{13} W/cm^2). The generated cyclohexane parent ions were trapped exclusively by adjusting radiofrequency voltages applied to the ion-trap electrodes. By repeating the ion generation and the mass-and charge-selective trapping around 150 times, $C_6H_{12}^+$ ions were accumulated in the ion trap. The stored $C_6H_{12}^+$ ions were irradiated with an intense femtosecond laser pulse (λ = 800 nm, $\Delta\tau$ = 40 fs) in the wide intensity range of 5.7×10^{11} ~ 8.0×10^{13} W/cm^2, and were decomposed into fragment species. The generated fragment ions were extracted from the ion trap by applying pulse high-voltage to the end-cap electrodes of the ion trap, and were recorded by TOF-MS. Because signals of the fragment ions were extremely weak, TOF mass spectral data recorded at each laser-shot were transferred into a personal computer (PC) 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 cyclohexane molecules, the electrodes of the ion trap were cooled down to about 77 K with liquid nitrogen and the background pressure of the vacuum chamber was kept to be about 3×10^{-7} Pa.

3. Results and Discussion

In order to investigate decomposition processes from $C_6H_{12}^+$, only the $C_6H_{12}^+$ species must be stored before the irradiation of the laser pulse that induces decomposition. The TOF-MS spectrum in Fig. 2 shows that the mass-

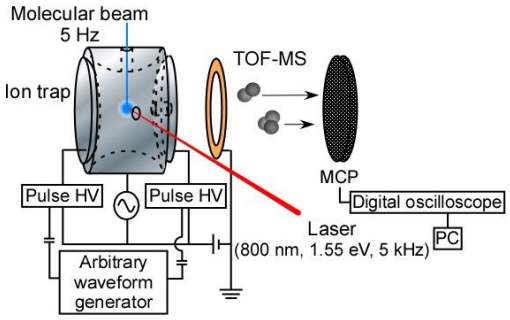

Fig. 1. The schematic of the ion trap TOF-MS.

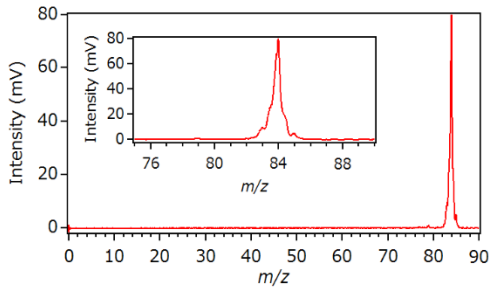

Fig. 2. The mass spectrum of stored ions in the ion trap after the mass selective ion accumulation for $C_6H_{12}^+$ (m/z = 84). Inset: the expanded view around m/z = 84.

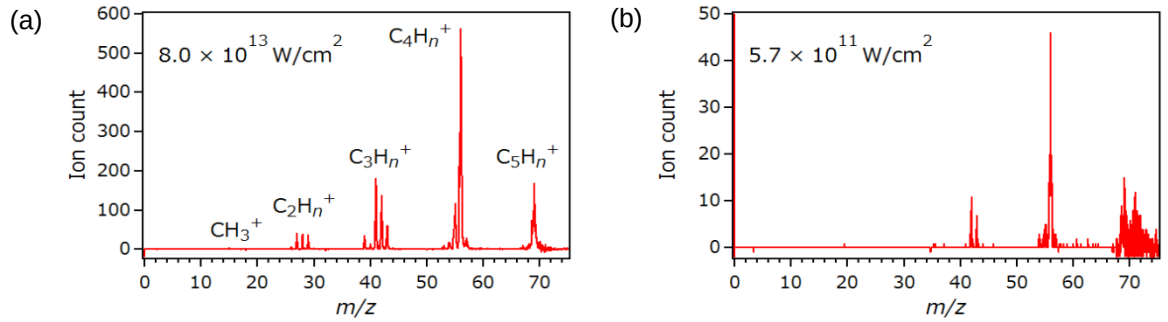

Fig. 3. The mass spectra of the fragment ions generated from the photodecomposition of $C_6H_{12}^+$ recorded when the laser field intensities were (a) 8.0×10^{13} W/cm^2 and (b) 5.7×10^{11} W/cm^2.

selective accumulation of $C_6H_{12}^+$ (m/z = 84) was achieved successfully before the irradiation of a laser pulse that induces the decomposition.

Figure 3 (a) shows a mass spectrum of fragment ions generated through the photodecomposition of the stored $C_6H_{12}^+$ obtained by the irradiation of a femtosecond laser pulse at the laser field intensity of 8.0×10^{13} W/cm^2. Various kinds of ion species, such as CH_3^+, $C_2H_n^+$ (n = 2~6), $C_3H_n^+$ (n = 3~8), $C_4H_n^+$ (n = 5~9), and $C_5H_n^+$ (n = 7~11), were observed as the product fragment ions. Figure 3 (b) shows a mass spectrum of fragment ions when the laser field intensity was 5.7×10^{11} W/cm^2. At this weaker field intensity, the signal intensities of small fragment ions, such as CH_3^+ and $C_2H_n^+$, decreased drastically relative to the signal intensity of $C_4H_8^+$ (m/z = 56), suggesting that absorption of a larger number of photons is necessary for generating the small fragment ions.

Figure 4 shows a double logarithmic plot of the yields of five different fragment ion species generated from $C_6H_{12}^+$ as a function of the laser field intensity. The slopes of the fitted lines for the larger size fragment ion species such as $C_5H_9^+$ (m/z = 69), $C_4H_8^+$ (m/z = 56), and $C_3H_6^+$ (m/z = 42) were in the range between 0.7 and 0.9, indicating that these ion species were produced from a parent ion via one-photon absorption, which is consistent with the mechanism proposed previously [1]. On the other hand, the slopes of the fitted lines for the smaller size fragment ion species such as $C_3H_5^+$ (m/z = 41) and $C_2H_4^+$ (m/z = 28) were in the range between 1.5 and 1.9, indicating that these ion species were produced from a parent ion via multiphoton absorption.

4. References

[1] H. Harada, S. Shimizu, T. Yatsuhashi, S. Sakabe, Y. Izawa, and N. Nakashima, "A key factor in parent and fragment ion formation on irradiation with an intense femtosecond laser pulse," Chem. Phys. Lett., **342**, 563-570 (2001).

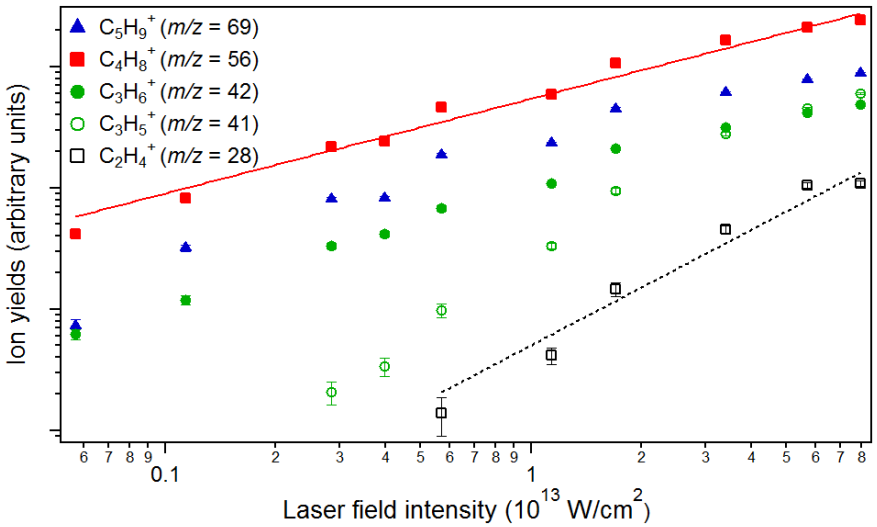

Fig. 4. The laser field intensity dependences of the yields of the five fragment ion species, $C_5H_9^+$(filled blue triangles), $C_4H_8^+$ (filled red squares), $C_3H_6^+$ (filled green circles), $C_3H_5^+$ (open green circles), and $C_2H_4^+$ (open black squares), produced by the decomposition of $C_6H_{12}^+$. Fitted straight lines for $C_4H_8^+$ (solid red line) and $C_2H_4^+$ (broken red line) are also shown.