Observation of Hydrogen Migration in Cyclohexane under an Intense Femtosecond Laser Field

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ABSTRACT: We experimentally demonstrate hydrogen migration in photoionization and photofragmentation processes of cyclohexane (C_6H_{12}) under a near-infrared (800 nm) intense femtosecond laser field by the dc-slice imaging technique, and the observation of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ can be regarded as direct evidence that chemical bond rearrangement processes associated with hydrogen migration occur in the dissociative ionization process of cyclohexane. We measure the sliced images of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ and calculate their corresponding kinetic energy release (KER) and angular distributions, and it is confirmed that high-KER components of these fragment ions result from two-body Coulomb explosion of the doubly charged parent ion $C_6H_{12}^{-2+}$ whereas low-KER components result from dissociative ionization of the singly charged parent ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$, and $C_3H_7^+$, which approach 4.5%, 4.0%, and 3.0%, respectively.



I. INTRODUCTION

The hydrogen migration process, in which a hydrogen atom or proton migrates from one site to another within a molecule, has attracted considerable attention in the last several years.¹⁻⁹ Such a process induced by an ultrashort intense laser field can occur very rapidly within the ultrashort laser pulse duration, which can result in deformation of molecular structure and rearrangement of chemical bonds and therefore can provide a new strategy to control chemical-bond-breaking and -forming processes.1-⁷ By now, the hydrogen migration process in various hydrocarbon molecules induced by intense femtosecond laser field has been experimentally demonstrated. For example, Xu and co-workers experimentally observed the singly charged fragment ions CH₃⁺ and CH₄⁺ in photoionization and photofragmentation process of allene (C_3H_4) , which confirmed that hydrogen atom or proton migrated between the methylene groups.⁸ Hoshina and co-workers experimentally demonstrated the ejection of fragment ion H_3^+ in several hydrocarbon molecular species without a methyl group, and these experimental results could illustrate that the hydrogen migration process in hydrocarbon molecules easily occurred under the intense femtosecond laser field.9

Cycloalkanes are the important constituents of most fuels and also are the major product of biomass conversion by pyrolysis.^{10,11} Because of the significant contribution in practical fuels, cyclohexane has been chosen as a representative cycloalkane in several surrogate mixtures of jet fuels.^{12,13} The photofragmentation process of cyclohexane under the intense femtosecond laser field has been widely studied in the past few decades. Castillejo and co-workers experimentally studied photofragmentation of cyclohexane by femtosecond laser pulses with the pulse duration of 200 fs and central wavelengths of 800 and 400 nm,¹⁴ and a number of fragment ions $CH_n^+-C_5H_m^+$

were observed, which was attributed to a predominant ionization followed by dissociation (ID) mechanism. They also performed a similar experiment by femtosecond laser pulses with the pulse duration of 50 fs and central wavelength of 800 nm,¹⁵ and the photofragmentation process was explained by field ionization and Coulomb explosion mechanism. Mebel and co-workers theoretically demonstrated Coulomb explosion processes on the ground-state potential energy surface of parent ion $C_6H_{12}^{3+16}$ and predicted the most favorable photofragmentation channels. Recently, Yamanouchi and co-workers experimentally studied the photofragmentation process of the singly charged parent ion $C_6H_{12}^+$ by ion trap time-of-flight (TOF) mass spectrometry,¹⁷ and the experimental results could well verify the conclusion proposed by Nakashia and co-workers that the molecular species like cyclohexane would exhibit significant fragmentation after ionization when the singly charged parent ion has a onephoton absorption band at the wavelength of ionization laser.¹⁸

The photoionization and photofragmentation process in cyclohexane is always accompanied by ultrafast motion of hydrogen atom or proton, which may result in hydrogen migration in cyclohexane.^{9,16} To our knowledge, hydrogen migration in cyclohexane has not been experimentally studied except for ejection of fragment ion H_3^+ ,⁹ which is also observed in our experiment. In this paper, we experimentally demonstrate hydrogen migration in the photoionization and photofragmentation process of cyclohexane under near-infrared (800 nm) femtosecond laser field by dc-slice imaging technique.¹⁹ Because there are no methyl groups in cyclo-

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hexane, the observation of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ can confirm that hydrogen atom or photon migrate among these methylene groups. The sliced images of fragment ions CH3⁺, C2H5⁺, and C3H7⁺ are measured, and their corresponding kinetic energy release (KER) and angular distributions are extracted and calculated. By observing the KER and angular distributions of these fragment ions, we confirm that Coulomb explosion (CE) of the doubly charged parent ion C₆H₁₂²⁺ and multiphoton dissociative ionization (DI) of the singly charged parent ion $C_6H_{12}^+$ coexist in our experiment, and high-KER components of these fragment ions result from two-body CE of the doubly charged parent ion $C_6H_{12}^{2+}$ whereas low-KER components result from DI of the singly charged parent ion C₆H₁₂⁺. Furthermore, the maximally attainable relative yields of fragment ions CH3⁺, C2H5⁺, and $C_3H_7^+$ are shown and discussed.

II. EXPERIMENTAL SECTION

The experiment is performed in our home-built dc slice imaging system, 2^{20-23} as schematically shown in Figure 1. The



Figure 1. Schematic diagram of our home-built dc slice imaging apparatus.

experimental apparatus mainly consists of two components, which are source chamber and main chamber. The background pressures for the source and main chambers are respectively 7.6 \times 10⁻⁷ and 4.6 \times 10⁻⁸ mbar and will increase to 8.5 \times 10⁻⁶ and 3.2×10^{-7} mbar when the molecular beam is introduced. The cyclohexane sample (Sinopharm Chemical Reagent Co., Ltd., 99.7+% purity) at room temperature is mixed with helium (He) gas at 1 atm with the ratio of 1:9 and introduced into the source chamber by pulsed valve to form a supersonic molecular beam, where the piezoelectric pulsed valve (general valve, Parker) has a orifice with diameter of 0.2 mm and operates at 100 Hz with a duration time of 100 μ s. The supersonic molecular beam is aligned by a skimmer with diameter of 1 mm and goes into the ionization region of the main chamber, and here the skimmer is mounted under the nozzle with the distance of 20 mm and used to separate the source chamber from the main chamber. The multistage ion lens is installed in the main chamber, which has the similar geometry described by Suits et al.¹⁹ The voltages applied on the electrodes are $U_1 = 2500$ V, $U_2 = 2178$ V, $U_3 =$ 2076 V, and $U_4 = 0$ V, which have been optimized according to the ion trajectory calculations simulated by SIMION 8.0 software. In such a condition, all ions with the same velocity vector can map on the same point of the detector. The temporal spread for ion cloud along TOF axis is about 350 ns,

and the measured kinetic energy range is 0.01-2.5 eV with corresponding resolution of 1-25 meV.

A Ti:sapphire chirped pulse amplification (CPA) laser system is used to generate intense femtosecond laser pulses with the pulse duration of 80 fs, maximum single-pulse energy of 3.5 mJ, repetition rate of 1 kHz and central wavelength of 800 nm (\sim 40 nm bandwidth), and the output laser pulses are focused into the main chamber by a quartz lens with focal length f = 40cm. A half-wave plate and a glan laser polarizer are placed in the laser beam path to change the input energy. In our experiment, the laser polarization direction is kept parallel to the detector plane by a half-wave plate. The laser intensity is calculated using formula of $I = (f \times \tau \times A)^{-1*}P$, where P, f, τ , and A respectively represent average power, repetition rate, pulse width, and focal area, and the calculated laser intensity is calibrated by the $Ar^{2+}/$ Ar⁺ ratio proposed by Guo et al.²⁴ In our experiment, the calibrated intensities at focal point are in the range of 2.7×10^{13} to $1.4 \times 10^{14} \text{ W/cm}^2$.

The laser and molecular beams are crossed perpendicularly in the middle of the repeller and extractor plates of a multistage ion lens, and the fragment ions produced by interaction of laser field with cyclohexane molecules are accelerated by ion lens and detected by two-stage microchannel plates (MCPs, Hamamatsu F2226-24) coupled to a P47 phosphor screen (PS) in a fieldfree region. The TOF mass spectra are acquired by a photomultiplier tube (PMT, Hamamatsu H7732-10) connected to a digital oscilloscope and transferred to a computer for storage and analysis. The dc sliced images of the ion cloud are obtained by an intensified charge coupled device (ICCD) camera (Princeton Instruments PI-MAXII, 512 \times 512 pixels) with time gate of 4 ns. All the timing sequence control is optimized by a digital delay pulse generator (DG535, Stanford Research System).

III. RESULTS AND DISCUSSION

Figure 2 shows TOF mass spectra of cyclohexane irradiated by femtosecond laser pulses with laser intensities of 4.1×10^{13} (a), 5.7×10^{13} (b), and 1.4×10^{14} W/cm² (c). Considering the laser pulse duration of 80 fs, it can be deduced that ionization



Figure 2. TOF mass spectra of cyclohexane molecules irradiated by intense femtosecond laser pulses with the laser intensities 4.1×10^{13} (a), 5.7×10^{13} (b), and 1.4×10^{14} W/cm² (c). The inset in Figure 2b is the enlarged mass spectra of fragment ions $C_2H_5^+$ and $C_3H_7^+$, and the inset in Figure 2c is the enlarged mass spectrum of fragment ions $C_5H_k^+$ (k = 1, 3, 5, 7, 9).

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followed by dissociation process is the responsible mechanism in our experiment. The observed fragmentation pattern of cyclohexane in Figure 2 is in agreement with the previous measurements.^{15,16} A number of fragment ions H^+ , H_2^+ , H_3^+ , C^{2+} , C^{3+} , CH_n^+ (n = 0-3), $C_2H_m^+$ (m = 0-5), $C_3H_i^+$ (i = 0-7), $C_4H_i^+$ (j = 0-8), and $C_5H_k^+$ (k = 1, 3, 5, 7, 9) are observed, which indicates that parent molecular ions are quite unstable and are easy to dissociate into fragment ions. With the increase of laser intensity, fragment ions containing a hydrogen element can further loss hydrogen. The generation of multicharged fragment ions C^{2+} and C^{3+} in higher laser intensity illustrates participation of CE processes in this experiment. Furthermore, the observation of fragment ions H_3^+ , CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ shows that hydrogen migration occurs in the dissociative ionization process of cyclohexane because no methyl groups are involved in cyclohexane, and the experimental results are similar to the ab initio studies of dissociative ionization of parent ion $C_6H_{12}^{3+}$, where the high mobility of hydrogen is verified due to low barriers to hydrogen migration.¹⁴ The ejection of fragment ion H₃⁺ has been experimentally observed and discussed with similar experimental conditions in previous studies,⁹ and therefore here we focus on exploring the formation mechanism of these fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ associated with hydrogen migration.

The hydrogen migration process induced by intense femtosecond laser field usually occurs in the range of tens of femtoseconds,¹⁻⁷ whereas the dissociation time of the C–C bond is at the subpicosecond time scale, and so the photofragmentation process of fragment ions is behind the hydrogen migration process. Therefore, we first assign the photofragmentation channel of these fragment ions CH₃⁺, $C_2H_5^+$, and $C_3H_7^+$, and the corresponding sliced images and KER distributions of these fragment ions are presented in Figure 3 with a laser intensity of 7.2×10^{13} W/cm². All KER distributions are fitted with multiple Gaussian functions, and peak KER values of the fitted Gaussian components are also labeled. It can be seen in Figure 3 that all these fragment ions are composed of both high- and low-KER components. Usually, fragment ions with high KER should result from the two-body CE process whereas those with low KER should result from the multiphoton DI process.^{20,25,26} Next we discuss photofragmentation channel of these fragment ions CH3⁺, C2H5⁺, and $C_3H_7^+$ on the basis of the two processes.

When gaseous molecules are exposed to intense femtosecond laser field, which can be multiply ionized to highly charged parent ions and then promptly dissociate into fragment ions by Coulomb repulsive force. In the two-body CE model, the two fragment ions separated by Coulomb repulsive force should satisfy the law of momentum conservation. That is to say, KERs of partner fragment ions X^{p+} and Y^{q+} should comply with the following relationship^{25,27}

$$\frac{\operatorname{KER}(X^{p^+})}{\operatorname{KER}(Y^{q^+})} = \frac{\operatorname{M}(Y^{q^+})}{\operatorname{M}(X^{p^+})}$$
(1)

where X and Y denote the partner fragment ions, *p* and *q* are the charge numbers of the two fragment ions, and *M* is the mass of the two fragment ions. On the basis of eq 1 and Figure 2, the partner fragment ions of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ can be assigned, which are fragment ions $C_5H_9^+$, $C_4H_7^+$, and $C_3H_5^+$, respectively. The slice images and corresponding KER distributions of these fragment ions $C_5H_9^+$, $C_4H_7^+$, and $C_3H_5^+$ are also presented in Figure 3. According to eq 1, the



Figure 3. dc sliced images of fragment ions CH₃⁺, C₃H₉⁺, C₂H₅⁺, C₄H₇⁺, C₃H₇⁺, and C₃H₅⁺ (a)–(f), and their corresponding KER distributions (g)–(l) with the laser intensity 7.2×10^{13} W/cm². The black circles are experimental data, and the red solid lines are simulated results with multipeak Gaussian functions.

two fragment ions CH_3^+ (m/q = 15, KER = 1.72 eV) and $C_5H_9^+$ (m/q = 69, KER = 0.39 eV) can be assigned to two-body CE process of the doubly charged parent ion $C_6H_{12}^{2+}$

$$C_6 H_{12}^{2+} \rightarrow C H_3^{+} + C_5 H_9^{+} (2.09 \text{ eV})$$
 (2)

Applying the same method, fragment ions $C_2H_5^+$ (m/q = 29, KER = 1.74 eV) and $C_4H_7^+$ (m/q = 55, KER = 0.90 eV), as well as fragment ions $C_3H_7^+$ (m/q = 43, KER = 1.34 eV) and $C_3H_5^+$ (m/q = 41, KER = 1.41 eV), can also be verified as a two-body CE process of the doubly charged parent ion $C_6H_{12}^{2+}$

$$C_6 H_{12}^{2+} \rightarrow C_2 H_5^{+} + C_4 H_7^{+} (2.61 \text{ eV})$$
 (3)

$$C_6 H_{12}^{2+} \rightarrow C_3 H_7^{+} + C_3 H_5^{+} (2.75 \text{ eV})$$
 (4)

Here, the energies of parentheses are the total translational release energy (TER) calculated by formula of TER = $(M(C_6H_{12})/M(Y^{q+}))*KER(X^{p+})$. As can be seen, all photo-fragmentation channels shown above come from the CE

process of the doubly charged parent ion $C_6H_{12}^{2+}$, but their TERs are different, which indicates that these photofragmentation channels should result from different precursor states of the doubly charged parent ion $C_6H_{12}^{2+}$, and this similar phenomenon has been experimentally demonstrated in methanol.^{28,29}

In addition to KER distribution, angular distribution of fragment ions is also an important method to assign photofragmentation channel, which can show instantaneous spatial distribution of fragment ions at the moment of CE process. For the two fragment ions from the same two-body CE process, their angular distributions should be consistent. Figure 4 shows angular distributions of partner fragment ions CH_3^+



Figure 4. Angular distributions of high-KER components of fragment ions CH_3^+ and $C_5H_9^+$ (a), $C_2H_5^+$ and $C_4H_7^+$ (b), and $C_3H_7^+$ and $C_3H_5^+$ (c) with the laser intensity 7.2 × 10¹³ W/cm².

and $C_5H_9^+$ (a), $C_2H_5^+$ and $C_4H_7^+$ (b), and $C_3H_7^+$ and $C_3H_5^+$ (c) with a laser intensity of 7.2 × 10¹³ W/cm². As expected, the two fragment ions originating from the same two-body CE channel exhibit a similar angular distribution, which can well confirm the above photofragmentation channel assignments.

In the molecular photofragmentation process under intense femtosecond laser field, neutral molecules can also be ionized to singly charged parent ions and then dissociate to a neutral fragment and a singly charged fragment ion by the rest laser energy or the repulsive states of singly charged parent ions. In this DI process, the KER of the fragment ion is usually relative low. Thus, fragment ion CH_3^+ (0.56 eV) could be assigned to the DI process of singly the charged parent ion $C_6H_{12}^+$

$$C_6 H_{12}^{+} \to C H_3^{+} + C_5 H_9$$
 (5)

Similarly, fragment ions $C_2H_5^+$ (0.14 eV) and $C_3H_7^+$ (0.08 eV) can also be respectively assigned to the DI process of the singly charged parent ion $C_6H_{12}^+$

$$C_6 H_{12}^{+} \rightarrow C_2 H_5^{+} + C_4 H_7$$
 (6)

$$C_6 H_{12}^+ \to C_3 H_7^+ + C_3 H_5$$
 (7)

To further confirm above photofragmentation channel assignments in DI process, we theoretically calculate the appearance energy of these channels (5)-(7) by GAUSSIAN 09 software packages³⁰ at the level MP2/6-311++G(d,p). Considering the laser bandwidth and wavelength in our experiment, the available energy can be calculated from the appearance energy. If the electron recoil is not considered, i.e., only two fragments

are involved in each photofragmentation channel, the KER value can be obtained from our experimental data in Figure 3. The appearance energy, available energy, and KER value in these channels (5)-(7) are listed in Table 1. One can see that

 Table 1. Appearance Energy, Available Energy, and KERs for

 Different DI Channels

| channel | appearance energy (eV) | available energy (eV) | KERs (eV) |
|---------|------------------------|-----------------------|-----------|
| (5) | 14.35 | 0.75-1.55 | 0.14-0.76 |
| (6) | 13.72 | 0-0.59 | 0.03-0.25 |
| (7) | 12.21 | 0-0.51 | 0.01-0.15 |

KER values of these channels are all in the range of available energies, which further indicate that low KER components of these fragment ions should result from DI process of the singly charged parent ion $C_6H_{12}^+$.

Because these fragment ions $C_3H_7^+$, $C_2H_5^+$, and CH_3^+ come from the CE process of the doubly charged parent ion $C_6H_{12}^{2+}$ and the DI process of the singly charged parent ion $C_6H_{12}^+$, we optimize the geometry structures of the doubly charged parent ion $C_6H_{12}^{2+}$ and the singly charged parent ion $C_6H_{12}^+$ from the structure of the neutral cyclohexane molecule C_6H_{12} by GAUSSIAN 09 software packages at the level of MP2/6-311++G(d,p), and the stable structures are shown in Figure 5.



Figure 5. Stable structures of doubly charged cyclohexane ion $C_6H_{12}^{2+}$, singly charged cyclohexane ion $C_6H_{12}^+$, and neutral molecule C_6H_{12} calculated by GAUSSIAN 09 software packages at the level MP2/6-311++G(d, p).

The equilibrium structure of parent ion $C_6H_{12}^{2+}$ shows that the six carbon atoms form a chain in trans—cis—trans conformation (3,1,2,2,1,3), which is quite different from that of neutral molecule C_6H_{12} with a cyclic geometry, and this significant structure change can also be observed in parent ion $C_6H_{12}^{3+.14}$. As can be seen, hydrogen migration has occurred during the ionization process. However, the equilibrium structure of parent ion $C_6H_{12}^{-+}$ still remains the cyclic geometry of neutral molecule C_6H_{12} , and no hydrogen migration occurs in the ionization process. These fragment ions CH_3^{++} , $C_2H_5^{++}$, and $C_3H_7^{-+}$ by CE and DI processes are observed in our experiment, which indicate that hydrogen migration before photofragmentation of parent ions $C_6H_{12}^{2+}$ and $C_6H_{12}^{++}$ still can occur.

The relative yield of fragment ions is an important parameter, which can show information about how difficult to produce fragment ions. In our experiment, the relative yields of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ are obtained by calculating the ratio of the corresponding signal intensity to the total ionization signal intensity. Figure 6 shows the relative yields of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ as the function of laser intensity. As can be seen, with an increase of laser intensity, all relative yields of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ show an increasing and then a decreasing process and reach maximum



Figure 6. Relative yields of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ as a function of laser intensity.

values at laser intensities of 1.0×10^{14} , 3.6×10^{13} , and 3.3×10^{13} W/cm², which correspond to 4.5%, 4.0%, and 3.0%, respectively. At higher laser intensity, the fast decrease of the relative yields of fragment ions $C_2H_5^+$ and $C_3H_7^+$ should be due to further dissociation of these fragment ions. These small fragment ions, such as H^+ , H_2^+ , C^{2+} , and C^{3+} , are observed at higher laser intensity, which can confirm our deduction.

IV. CONCLUSION

The hydrogen migration in cyclohexane C₆H₁₂ under an intense femtosecond laser field has been experimentally investigated by the dc-slice imaging technique. The observation of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ could be regarded as direct evidence that hydrogen migration occurs in the dissociative ionization process of cyclohexane because no methyl groups are involved in cyclohexane. By determining KER and angular distributions of fragment ions CH₃⁺, C₂H₅⁺ and $C_3H_7^+$ and their partner fragment ions $C_5H_9^+$, $C_4H_7^+$, and C₃H₅⁺, we confirm that high-KER components of these fragment ions came from the CE process of the doubly charged parent ion $C_6H_{12}^{2+}$, whereas low-KER components came from the DI process of the singly charged parent ion $C_6H_{12}^+$. In addition, the maximally attainable relative yields of fragment ions CH_3^+ , $C_2H_5^+$, and $C_3H_7^+$ were shown to be 4.5%, 4.0%, and 3.0%, respectively. These experimental results are useful to understand hydrogen migration in hydrocarbon molecules under an intense femtosecond laser field and are expected to be significant for controlling the photochemical reaction.

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Notes

The authors declare no competing financial interest.

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