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Investigation of Vacuum Ultraviolet Photoionization of Methylcyclohexane in Energy Region of 9–15.5 eV

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Vacuum ultraviolet (VUV) photoionization and photodissociation of methylcyclohexane have been studied utilizing a reflectron time-of-flight mass spectrometer (RTOF-MS) with synchrotron radiation source. Photoionization efficiency curves (PIEs) of molecule ion $C_7H_{14}^+$ and fragment ions $C_7H_{13}^+$, $C_6H_{11}^+$, $C_6H_{10}^+$, $C_5H_{10}^+$, $C_5H_9^+$, $C_4H_8^+$, $C_4H_7^+$, and $C_3H_5^+$ were observed. The ionization energy of methylcyclohexane was measured to be (9.80 ± 0.03) eV, and appearance energies of fragment ions were determined from the PIEs. Optimized structures of transitional states, intermediates and product ions were characterized at the B3LYP/6-31G(d) level and the energies were calculated using G3B3 method. Formation channels of dominating fragment ions were proposed. Intramolecular hydrogen migrations and carbon ring-opening were the foremost processes in fragmentation pathways of methylcyclohexane.

Key words: Methylcyclohexane, Photoionization and photodissociation, Synchrotron radiation source, Reflectron time-of-flight mass spectrometer

I. INTRODUCTION

Cycloalkanes and alkyl-cycloalkanes are an important class of organic compounds, found in gasoline ($\sim 10\%$), diesel ($\sim 35\%$) and aviation fuels ($\sim 20\%$) [1–3]. Cyclopentane, cyclohexane and alkyl substituted derivatives are common hydrocarbons in petroleum products [4, 5]. As concerns about rising fuel prices have intensified, it is expected to discover alternative sources of fuels, such as cycloalkanes. The cycloalkanes have high calorific value, low freezing point, and explosion resistance between the normal hydrocarbon and the isomeric hydrocarbon.

Methylcyclohexane (MCH) has the methyl group in either a polar or an equatorial position. Steric interactions of MCH are similar to those of *n*-paraffins in various configurations. It is also found that the presence of a ring structure contributes to the activation energy barrier of the isomerization reaction [6, 7]. As we all know, MCH has been a good choice of candidate component to be applied largely into the typical representative in jet fuel surrogates [8–11]. High temperature oxidation and pyrolysis of MCH have been investigated by using a flow reactor [12–16]. Recently, Rotavera *et al.* [17] studied ignition behaviors of pure and blended

MCH, and reported the ignition delay time dependence of MCH and linear alkanes/cycloalkanes through experimental and modeling studies. Hong *et al.* [18] investigated the influence of molecular structures on ignition behavior in the case of the cycloalkanes, using the predicted H_2O plateau levels of different mechanisms. A similar flux analysis was performed for MCH oxidation at certain temperature, pressure and consumption with O_2 stoichiometric mixture. They proposed that two major pathways of unimolecular dissociation reactions could occur in the photoionization and photodissociation of MCH, one is the methyl group breaking off from the six-membered ring, and the other involves ring-opening. Hence, a better understanding of the energetics for alkyl-cycloalkanes is clearly desirable.

There are few photoionization and photodissociation studies on methylcyclohexane in the gas phase. Pottier *et al.* [19] reported the ionization potentials of cycloalkyl free radicals and cycloalkanes by electron impact and mass spectrometry. The $C_6H_{11}^+$ ion from the dissociation ionization of MCH was identified as a cyclohexyl ion by simple bond fission.

In the present work, the dissociative photoionization of methylcyclohexane was performed using reflectron time-of-flight mass spectrometry with synchrotron radiation source. By measuring the photoionization efficiency curves of mother ion and main fragment ions, the ionization energy (IE) of MCH and appearance energies (AEs) of fragment ions were obtained. By combining with theoretical calculations, possible mechanisms on

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the dissociation photoionization of MCH were discussed.

II. EXPERIMENTAL METHOD

The experiments were performed on the Atomic and Molecular Physics Beamline (BL09U), using the synchrotron radiation from the 800-MeV electronic storage ring and a flow of 360 mA at Hefei National Synchrotron Radiation Laboratory. The experimental apparatus has been described elsewhere [20–27], and would be briefly introduced here. The high-resolution spherical grating monochromator was designed to provide the VUV light of 8–124 eV in the combination with the higher harmonics of the undulator. With the energy resolution ($E/\Delta E$) of 3000 at 15 eV, the average photon flux was approximately 2×10^{13} photon/s at 360 mA, the spot size was about $0.5 \text{ mm} \times 0.8 \text{ mm}$. Energy calibration was performed using well-identified rare gas photoionization potentials. During the experiment, photocurrent was measured by using a photodiode and a picoammeter, Ar (5.4 Torr) was used as the filter gas to eliminate interference from higher harmonics.

The sample of methylcyclohexane (purity $\geq 99.5\%$) was obtained from Aladdin, and used directly without further processing. Methylcyclohexane was placed in a specific liquid sample chamber that was controlled by the needle valves into the molecular expansion chamber through a 6 mm diameter stainless steel tube. Helium was selected as the carrier gas with the purity of 99.99%, and the experimental pressure was about 1.0 bar. After the sample molecules entered the beam source chamber, the methylcyclohexane gas molecules were supersonically expanded into the ionization chamber through a 70- μm diameter nozzle and a 1.5 mm diameter skimmer. Subsequently, the cold swept molecular beam was injected vertically into the ionization zone that intersected the VUV beam. The resulting ions were then subjected to mass analysis using a home-made RTOF-MS. Mass spectra of methylcyclohexane and PIE curves of fragment ions were obtained in the energy range of 9.0–15.5 eV. A monochromator with a scanning step size of 0.03 eV was utilized, at the energy accumulation time per step of 60 s, to obtain the PIE of MCH and the appearance potentials of fragment ions.

III. THEORETICAL METHOD

In this research, density functional theory (DFT) is used to investigate potential energy surfaces on the photodissociation and isomerization of methylcyclohexane. Optimized structures and energies are calculated using Gaussian 09, Revision A.1 program at the B3LYP level on the 6-31G(d) basis set. Comparing with existing experimental values and previous research results, we infer possible structures and dissociation channels of frag-

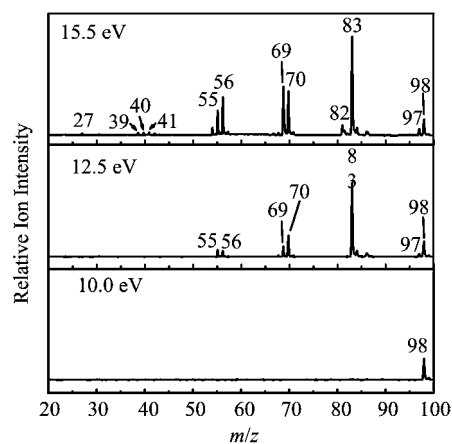


FIG. 1 Photoionization mass spectra of MCH at different energies of 10.0, 12.5, and 15.5 eV, respectively.

ment ions. The detailed formation of fragment ions is further deduced by locating the transition states and intermediates involved in the channels.

DFT is currently the most widely theory used in the fields of materials, biochemistry, and chemistry [28]. Although specific functionalities have not yet been clarified [29], various alternatives have been successfully implemented in many popular computational codes. B3LYP is the most famous hybrid generalized gradient approximation (GGA) and has been widely used in almost all chemical fields. It is a hybrid of fine Hartree-Fock exchange with local and semilocal exchanges and related terms on the basis of adiabatic connections [30]. It is calculated about the harmonic vibration frequencies for the zero-point correction at the B3LYP/6-31G(d) level. A Gaussian 09 investigation using B3LYP method is carried out to measure the various fragments of MCH. In addition, G3B3 method is used to obtain energetic calculations and heats of formation at 298 K are calculated. The stabilities, structures and thermochemical properties of fragment ions are studied and discussed. All of these calculations are performed using the Gaussian 09 program suites from the Supercomputing Center of University of Science and Technology of China [31].

IV. RESULTS AND DISCUSSION

A. Photoionization mass spectra of methylcyclohexane

FIG. 1 shows photoionization mass spectra of MCH at different energies of 15.5, 12.5, 10.0 eV. Only the parent ion at $m/z=98$ appears at the low energy (10.0 eV), which is produced by the removal of one of electrons in the MCH. Fragment ions are gradually formed with the increasing of photon energy. At the photon energy of 12.5 eV, one strong fragment ion at $m/z=83$ ($\text{C}_6\text{H}_{11}^+$) is observed, which is deduced by loss of CH_3 group directly from the parent ion, and more fragments

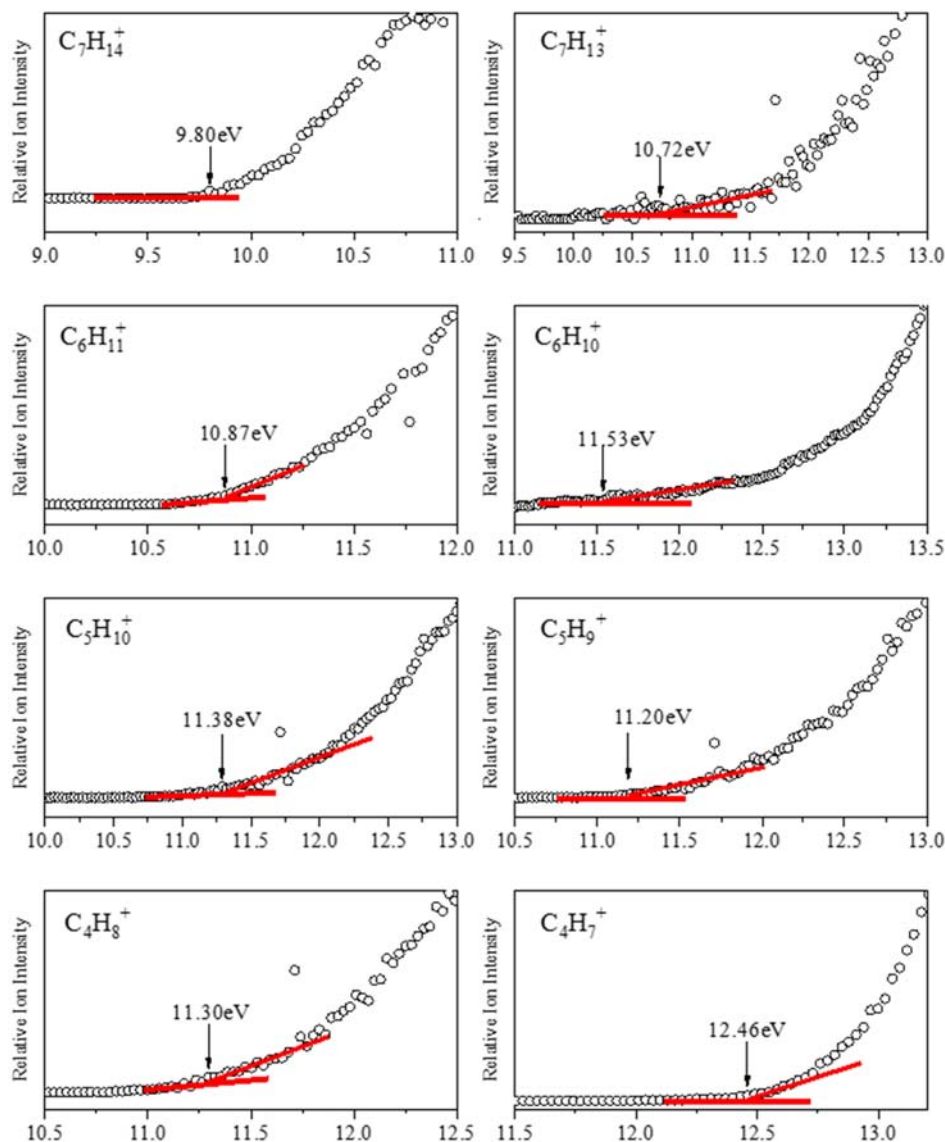


FIG. 2 Normalized PIE curves of the parent ion and major fragment ions in the dissociative photoionization of MCH.

at $m/z=97$ ($C_7H_{13}^+$), 70 ($C_5H_{10}^+$), 69 ($C_5H_9^+$), 56 ($C_4H_8^+$), and 55 ($C_4H_7^+$) are detected. With the photon energy rising to 15.5 eV, the above fragment ions are explicitly stronger in the mass spectrum. Smaller peaks for fragment ions at $m/z=82$ ($C_6H_{10}^+$), 54 ($C_4H_6^+$), 41 ($C_3H_5^+$), 40 ($C_3H_4^+$), 39 ($C_3H_3^+$), and 27 ($C_2H_3^+$) are also observed. All fragment ions observed are considered to be dissociated from the parent ion because no signal with the mass greater than $C_7H_{14}^+$ ($m/z=98$) is found. The fragment peak of $m/z=83$ ($C_6H_{11}^+$) has the highest intensity in the photodissociation process of MCH, which is indicated that the $C_6H_{11}^+$ ion is the dominant dissociation channel of methylcyclohexane cation by loss of a methyl above the appearance energy.

In the study, with automatic scanning of the photon energies with monochromatized synchrotron radi-

ation, the PIE curves of methylcyclohexane cation and dominating fragment ions were obtained by integrating the peak areas to normalize the recorded photon flux at each photon energy. FIG. 2 shows the normalized PIE curves of main product ions in the dissociative photoionization of MCH. Without considering the distribution from the parent molecule thermal energy, only the above-mentioned supersonic expansion of the nozzle was considered. Here, the experimental IE value of parent molecule was determined to be (9.80 ± 0.03) eV, which was well consistent with the previous values of (9.62 ± 0.05) eV [32], (9.69 ± 0.15) eV [33], (9.76 ± 0.03) eV [34], (9.85 ± 0.03) eV [35], (9.70 ± 0.0025) eV [36] obtained from photoelectron spectroscopy or photoionization/mass-analyzed threshold ionization (MATI) mass spectrometry. With the aid of G3B3 method at the B3LYP/6-31G(d) level,

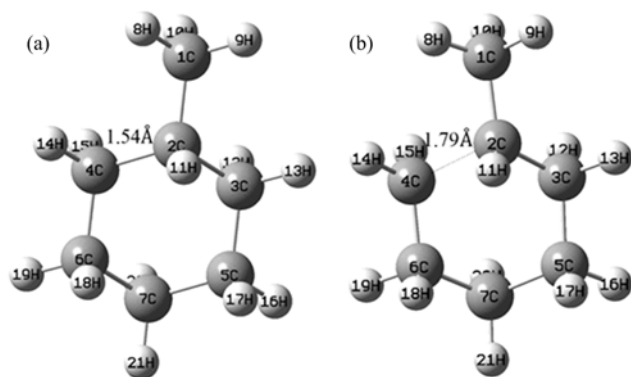


FIG. 3 Geometric constructions of (a) the neutral MCH and (b) the ionized parent molecule.

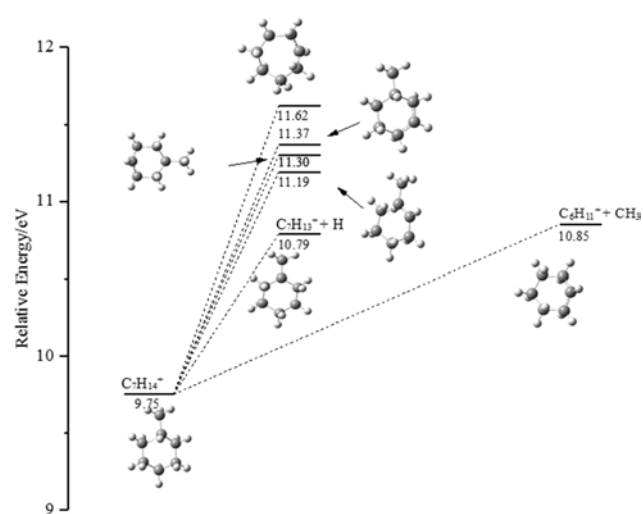


FIG. 4 Formation pathways of $C_7H_{13}^+$ and $C_6H_{11}^+$ calculated at the B3LYP/6-31G(d) level.

the theoretical IE value of MCH was calculated to be 9.75 eV, which is in accordance with our experimental result. Methylcyclohexane is a monosubstituted cyclohexane which has one branch by attaching a methyl group to one carbon of the cyclohexane ring. FIG. 3 shows optimized geometries of the neutral MCH and the ionized parent molecule. It was found that the bond length between C2 and C4 increases from 1.54 Å to 1.79 Å, which suggests that the six-membered ring would be easier to open for further dissociation at an elevated energy.

B. Dissociation mechanisms

In the case of the dissociative photoionization, fragment ions are generally considered to be formed from parent molecule ions. Theoretical appearance energies of fragment ions are actually enthalpy changes of the dissociative processes. With theoretical calculations

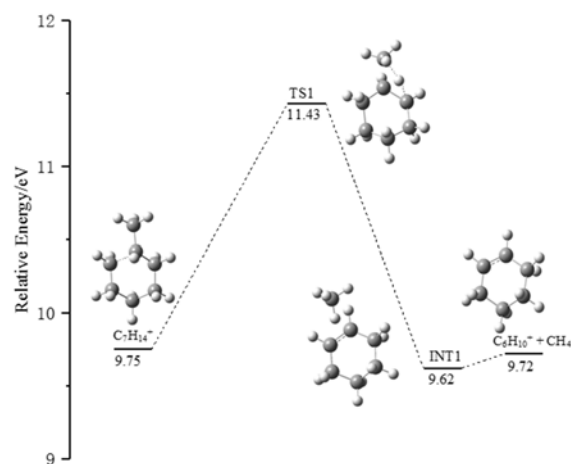


FIG. 5 Formation pathway of $C_6H_{10}^+$ calculated at the B3LYP/6-31G(d) level.

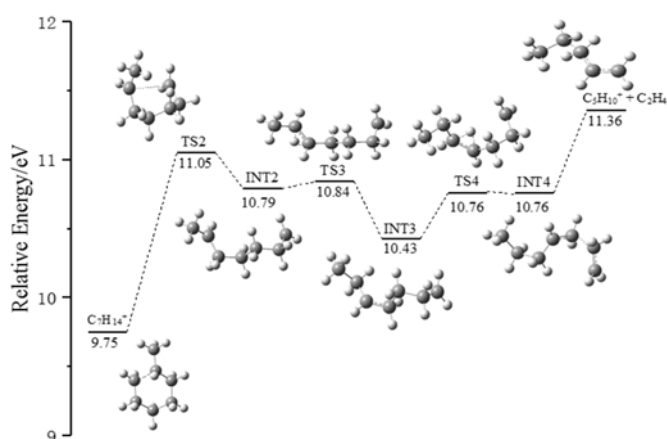


FIG. 6 Formation pathway of $C_5H_{10}^+$ calculated at the B3LYP/6-31G(d) level.

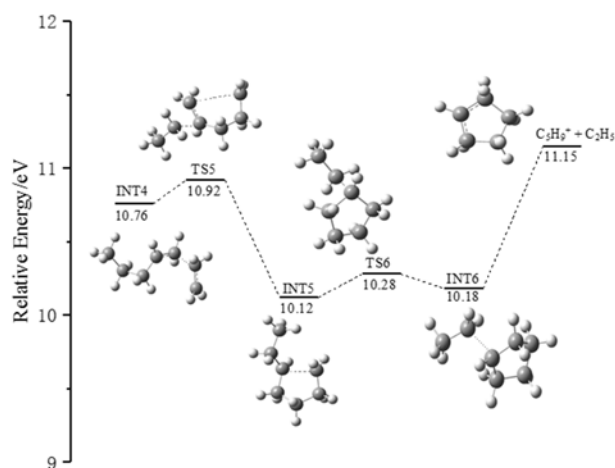


FIG. 7 Formation pathway of $C_5H_9^+$ calculated at the B3LYP/6-31G(d) level.

TABLE I Theoretical and experimental values of ionization energy and appearance energies for main fragment ions from the dissociative photoionization of MCH.

m/z Ions	IE/AE			Possible dissociation pathways
	Experiment	Calculated	Reference	
98 $C_7H_{14}^+$	9.80 ± 0.03	9.75	9.62 [32], 9.69 [33], 9.76 [34], 9.85 [35], 9.70 [36]	$C_7H_{14}^+ \rightarrow C_7H_{14}^+ + e$
97 $C_7H_{13}^+$	10.72 ± 0.06	10.79		$C_7H_{14}^+ \rightarrow C_7H_{13}^+ + H$
83 $C_6H_{11}^+$	10.87 ± 0.05	10.85	10.95 [19]	$C_7H_{14}^+ \rightarrow C_6H_{11}^+ + CH_3$
82 $C_6H_{10}^+$	11.53 ± 0.08	11.43		$C_7H_{14}^+ \rightarrow C_6H_{10}^+ + CH_4$
70 $C_5H_{10}^+$	11.38 ± 0.05	11.36		$C_7H_{14}^+ \rightarrow C_5H_{10}^+ + C_2H_4$
69 $C_5H_9^+$	11.20 ± 0.05	11.15		$C_7H_{14}^+ \rightarrow C_5H_9^+ + C_2H_5$
56 $C_4H_8^+$	11.30 ± 0.05	11.36		$C_7H_{14}^+ \rightarrow C_4H_8^+ + C_3H_6$
55 $C_4H_7^+$	12.46 ± 0.03	12.50		$C_7H_{14}^+ \rightarrow C_4H_7^+ + C_2H_4 + CH_3$

using G3B3 at the B3LYP/6-31G(d) level, formation channels of major fragment ions of methylcyclohexane are established in detail. FIGs. 4–7 show optimized geometric structures and energies for given main product fragment ions, as well as transitional states, intermediates and product ions. In general, photodissociation mechanisms have been proposed in two cases: one is direct single bond splitting and the other is indirect bond splitting through transition states and intermediates.

1. Formation pathways of $C_7H_{14}^+$ and $C_7H_{13}^+$

The mother ion $C_7H_{14}^+$ is directly obtained by dropping an electron from the molecule of MCH, which has a chair-like conformation. With the aid of theoretical calculations at the B3LYP/6-31G(d) level, the most charge distribution is on the C2 atom connecting the methyl group. Thus, the IE of MCH is calculated to be 9.75 eV, well consistent with our experiment value (9.80 ± 0.03) eV. The corresponding results are shown in Table I.

For $C_7H_{13}^+$ ion, there are five types to remove one hydrogen atom, which are hydrogen removals from C1, C2, C3, C5, and C7. Theoretical AEs of $C_7H_{13}^+$ are calculated to be 11.62 eV (H-loss from C1), 10.79 eV (H-loss from C2), 11.19 eV (H-loss from C3), 11.37 eV (H-loss from C5), and 11.30 eV (H-loss from C7), respectively, as shown in FIG. 4. The theoretical AE value of hydrogen removal from C2 is in good accordance with our experiment result of (10.72 ± 0.06) eV, which indicates the most possible channel of $C_7H_{13}^+$ ion is a hydrogen elimination from C2 site of molecular ion.

2. Formation pathways of $C_6H_{11}^+$ and $C_6H_{10}^+$

As the dominant dissociation fragment, the $C_6H_{11}^+$ ion (cyclohexyl cation) is produced from the dissociation of $C_7H_{14}^+$ via releasing CH_3 group directly, as

shown in FIG. 4. The calculated AE value of 10.85 eV for $C_6H_{11}^+$ ion is in good agreement with our experimental result of (10.87 ± 0.05) eV and the previous value of 10.95 eV [19]. The formation mechanism of $C_6H_{11}^+$ ion is direct dissociation from molecular ion.

The formation channel of $C_6H_{10}^+$ ion is proposed by loss of the neutral CH_4 group, as shown in FIG. 5. Firstly, hydrogen transfers from C4 to C1, which has a stable vibration between two C atoms. This process forms INT1 via TS1 with the energy barrier of 1.68 eV. Afterwards, the product ion $C_6H_{10}^+$ is yielded with the loss of CH_4 group through the cleavage of C1–C2 bond. The calculated AE value for $C_6H_{10}^+$ ion is 11.43 eV, which is consistent with the experimental value (11.53 ± 0.08) eV.

3. Formation pathway of $C_5H_{10}^+$ and $C_5H_9^+$

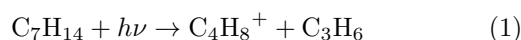
For the formation channel of $C_5H_{10}^+$ ion, the six-membered ring of methylcyclohexane cation is opened firstly to form INT2 via TS2 with an energy barrier of 1.30 eV. Then, hydrogen migration from C3 to C2 produces INT3 via transition state TS3. Subsequently, INT4 is generated via transition state TS4 undergoing hydrogen transfer from C5 to C3. After two hydrogen shifts, the cleavage of C6–C7 bond can produce $C_5H_{10}^+$ ion with $CH_3CH_2CH_2CH=CH_2$ geometry and C_2H_4 neutral group, as shown in FIG. 6. The AE value of $C_5H_{10}^+$ ion is calculated to be 11.36 eV, which is in good consistence with the experimental value of (11.38 ± 0.05) eV.

The formation channel of $C_5H_9^+$ is considered by breaking of C2–C3 bond from the structure of INT4 (FIG. 7). The AE value for $C_5H_9^+$ (loss C_2H_5 group from INT4) is calculated to be 12.19 eV, which is much higher than the experimental value of (11.20 ± 0.05) eV. This suggests there may be another channel for the formation of $C_5H_9^+$. With the bond length of C2–C3 increasing and C2–C5 getting shortened, transition state TS5 is formed from INT4 to generate INT5 with the

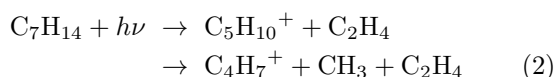
energy barrier of 0.16 eV. INT6 via transition state is TS6. The cleavage of C2–C5 bond from INT6 produces cyclopentyl cation $C_5H_9^+$ ion with five-membered ring and C_2H_5 group, as shown in FIG. 7. The calculated AE value 11.15 eV is in good agreement with the experimental result of 11.20 eV.

4. Formation pathway of $C_4H_8^+$ and $C_4H_7^+$

From the perspective of $C_4H_8^+$ ion, it is supposed that INT2 (after the six-membered ring opened) produces $C_4H_8^+$ ion ($CH_3CH_2CH=CH_2^+$) and releases C_3H_6 group ($CH_3CH=CH_2$) by the bond fission of C5–C7 bond. The theoretical AE value of the direct bond cleavage is calculated to be 11.36 eV, which is in excellent consistence with the obtained experimental value (11.30 ± 0.05) eV. Possible pathways are given in the following chemical reaction (1).



The $C_4H_7^+$ ion ($CH_3CH=CH=CH_2^+$) is envisioned to be evolved from the $C_5H_{10}^+$ ion via breaking CH_3 group. The calculated AE value of $C_4H_7^+$ ion is 12.50 eV, which agrees well with our experimental result of (12.46 ± 0.03) eV. The pathway is reasonable and effective for this proposed dissociation way, which is shown as the following dissociation reaction (2).



V. CONCLUSION

In this study, we have investigated the dissociative photoionization of MCH in the energy range of 9–15.5 eV using reflectron TOF-MS with synchrotron radiation source under supersonic expansion conditions. From their photoionization efficiency curves, AEs values for fragment ions at $m/z=97$ ($C_7H_{13}^+$), 83 ($C_6H_{11}^+$), 82 ($C_6H_{10}^+$), 70 ($C_5H_{10}^+$), 69 ($C_5H_9^+$), 56 ($C_4H_8^+$), and 55 ($C_4H_7^+$) are derived to be (10.72 ± 0.06) eV, (10.87 ± 0.05) eV, (11.53 ± 0.08) eV, (11.38 ± 0.05) eV, (11.20 ± 0.05) eV, (11.30 ± 0.05) eV, and (12.46 ± 0.03) eV, respectively. With the aid of theoretical calculations of hybrid generalized gradient approximation at the B3LYP/6-31G(d) level, dissociative photoionization mechanisms of MCH are proposed for the first time. Intramolecular hydrogen migrations and carbon ring-opening are the foremost processes in fragmentation pathways of methylcyclohexane.

VI. ACKNOWLEDGEMENTS

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- [1] S. Dooley, J. Heyne, S. H. Won, P. Dievert, Y. G. Ju, and F. L. Dryer, *Energy Fuels* **28**, 7649 (2014).
- [2] N. Hansen, T. Kasper, S. J. Klippenstein, P. R. Westmoreland, M. E. Law, C. A. Taatjes, K. Kohse-Höinghaus, J. Wang, and T. A. Cool, *J. Phys. Chem. A* **111**, 4081 (2007).
- [3] E. J. Silke, W. J. Pitz, C. K. Westbrook, and M. Ribaucour, *J. Phys. Chem. A* **111**, 3761 (2007).
- [4] A. Agosta, *M. S. Dissertation*, Philadelphia: Drexel University, (2002).
- [5] J. T. Farrell, N. P. Cernansky, F. L. Dryer, C. A. Hergart, C. K. Law, R. M. McDavid, C. J. Mueller, A. K. Patel, and H. Pitsch, *SAE Technical Papers* **1**, 201 (2007).
- [6] W. J. Pitz, C. V. Naik, T. N. Mhaoldúin, C. K. Westbrook, H. J. Curran, J. P. Orme, and J. M. Simmie, *Proc. Combust. Inst.* **31**, 267 (2007).
- [7] F. Buda, B. Heyberger, R. Fournet, P. A. Glaude, V. Warth, and F. Battin-Leclerc, *Energy Fuels* **20**, 1450 (2006).
- [8] Z. D. Wang, L. L. Ye, W. H. Yuan, L. D. Zhang, Y. Z. Wang, Z. J. Cheng, F. Zhang, and F. Qi, *Combust. Flame* **161**, 84 (2014).
- [9] A. T. Holley, Y. Dong, M. G. Andac, and F. N. Egolopoulos, *Proc. Comb. Inst.* **144**, 448 (2006).
- [10] T. Bieleveld, A. Frassoldati, A. Cuoci, T. Faravelli, E. Ranzi, U. Niemann, and K. Seshadri, *Proc. Combust. Inst.* **32**, 493 (2009).
- [11] C. V. Naik, W. J. Pitz, M. Sjöberg, J. E. Dec, J. Orme, H. J. Curran, J. M. Simmie, and C. K. Westbrook, *SAE Trans.* **114**, 1381 (2005).
- [12] J. P. Orme, H. J. Curran, and J. M. Simmie, *J. Phys. Chem. A* **110**, 114 (2006).
- [13] J. M. Simmie, *Prog. Energy Combust. Sci.* **29**, 599 (2003).
- [14] S. Zeppieri, K. Brezinsky, and I. Glassman, *Combust. Flame* **108**, 266 (1997).
- [15] M. K. Liszka and K. Brezinsky, *Fuel* **237**, 245 (2019).
- [16] T. Bissoonauth, Z. D. Wang, S. Y. Mohamed, J. Y. Wang, B. J. Chen, A. Rodriguez, O. Frottier, X. Y. Zhang, Y. Zhang, C. C. Cao, J. Z. Yang, O. Herbinet, F. Battin-Leclerc, and S. M. Sarathy, *Proc. Combust. Inst.* **37**, 409 (2019).
- [17] B. Rotavera and E. L. Petersen, *Proc. Combust. Inst.* **34**, 435 (2013).
- [18] Z. Hong, K. Y. Lam, D. F. Davidson, and R. K. Hanson, *Combust. Flame* **158**, 1456 (2011).
- [19] R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Am. Chem. Soc.* **83**, 3204 (1961).
- [20] M. Q. Cao, J. Chen, W. Z. Fang, Y. Q. Li, S. L. Ge, X. B. Shan, F. Y. Liu, Y. J. Zhao, Z. Y. Wang, and L. S. Sheng, *Eur. J. Mass Spectrom.* **20**, 419 (2014).
- [21] G. B. Chu, J. Chen, F. Y. Liu, X. B. Shan, J. G. Han, and L. S. Sheng, *Chem. Phys.* **416**, 26 (2013).

- [22] F. Y. Liu, C. X. Li, G. H. Wu, H. Gao, F. Qi, L. S. Sheng, Y. W. Zhang, S. Q. Yu, S. H. Chien, and W. K. Li, *J. Phys. Chem. A* **105**, 2973 (2001).
- [23] Y. L. Song, J. Chen, M. M. Ding, B. Wei, M. Q. Cao, X. B. Shan, Y. J. Zhao, C. Q. Huang, L. S. Sheng, and F. Y. Liu, *J. Mol. Struct.* **1094**, 83 (2015).
- [24] Y. Xie, L. L. Cao, Q. Zhang, J. Chen, G. B. Chu, Y. J. Zhao, X. B. Shan, F. Y. Liu, and L. S. Sheng, *Chin. J. Chem. Phys.* **25**, 379 (2012).
- [25] Z. H. Li, Y. P. Yu, X. Lin, J. Chen, H. Zhang, Y. B. Li, H. H. Wang, Q. H. Meng, R. R. Sun, X. B. Shan, F. Y. Liu, and L. S. Sheng, *Chin. J. Chem. Phys.* **31**, 619 (2018).
- [26] M. Wang, J. Chen, W. F. Fei, Z. H. Li, Y. P. Yu, X. Lin, X. B. Shan, F. Y. Liu, and L. S. Sheng, *Chin. J. Chem. Phys.* **31**, 379 (2018).
- [27] J. Chen, M. Q. Cao, B. Wei, M. M. Ding, X. B. Shan, F. Y. Liu, and L. S. Sheng, *J. Mass Spectrom.* **51**, 169 (2016).
- [28] R. H. Hertwig and W. Koch, *Chem. Phys. Lett.* **268**, 345 (1997).
- [29] S. N. Maximoff and G. E. Scuseria, *Chem. Phys. Lett.* **390**, 408 (2004).
- [30] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).
- [31] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, H. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. M. Martain, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision A.1*, Wallingford, CT: Gaussian, Inc., (2009).
- [32] J. L. Holmes and F. P. Lossing, *Org. Mass Spectrom.* **26**, 537 (1991).
- [33] M. Meot-Ner, L. W. Sieck, and P. Ausloos, *J. Am. Chem. Soc.* **103**, 5342 (1981).
- [34] S. Rang, P. Paldoia, and A. Talvari, *Eesti. NSV Tead. Akad. Toim.* 354 (1974).
- [35] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer* **2**, 369 (1962).
- [36] S. Han, H. S. Yoo, D. Ahn, Y. S. Choi, and S. K. Kim, *Chem. Phys. Lett.* **518**, 38 (2011).