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ARTICLE

Theoretical Investigation on Photoionization and Dissociative Photoionization of Toluene

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The photoionization and dissociation photoionization of toluene have been studied using quantum chemistry methods. The geometries and frequencies of the reactants, transition states and products have been performed at B3LYP/6-311++G(d,p) level, and single-point energy calculations for all the stationary points were carried out at DFT calculations of the optimized structures with the G3B3 level. The ionization energies of toluene and the appearance energies for major fragment ions, $C_7H_7^+$, $C_6H_5^+$, $C_5H_6^+$, $C_5H_5^+$, are determined to be 8.90, 11.15 or 11.03, 12.72, 13.69, 16.28 eV, respectively, which are all in good agreement with published experimental data. With the help of available published experimental data and theoretical results, four dissociative photoionization channels have been proposed: $C_7H_7^+$+H, $C_6H_5^+$+CH_3, $C_5H_6^+$+C_2H_2, $C_5H_5^+$+C_2H_2+H. Transition structures and intermediates for those isomerization processes are determined in this work. Especially, the structures of $C_5H_6^+$ and $C_5H_5^+$ produced by dissociative photoionization of toluene have been defined as chain structure in this work with theoretical calculations.

Key words: Quantum chemical calculations, Toluene, Dissociative photoionization mechanism, Density functional theory, Transition states

I. INTRODUCTION

Aromatic hydrocarbons such as benzene, toluene, and xylene are major components of volatile organic compounds (VOCs) in urban areas, with toluene being the most abundant aromatic hydrocarbon among them, which play an important role in the formation of secondary organic aerosols [1−4]. Moreover, toluene has strong stimulation to eyes, skin, mucous membrane and respiratory system. Toluene also takes a part in reactions to promote photochemical smog and other local atmospheric effects, which may contribute significantly to ozone formation in the troposphere [5−9]. Therefore, the understanding of the process for dissociative photoionization of toluene is needed for evaluating the risks involved in aromatic compounds.

The photoionization of toluene has been studied by various experimental methods. By using electron impact techniques, Mcloughlin *et al.* [10, 11] obtained the ionization energy (IE) of toluene and the appearance energy (AE) of $C_7H_7^+$, which are 8.82 and 10.71 eV, respectively. Lifshitz *et al.* [12, 13] investigated two dissociative photoionization channels of $C_7H_7^+$, through time resolved photoionization mass spectrometry (TPIMS) by combining with *ab initio* calculations, in which the AEs of $C_7H_7^+$ being determined to be 11.1 and 10.7 eV at T=0 and T=298 K, respectively. Shaw *et al.* [14] used three experimental techniques (photoabsorption, photoelectron and photoion spectroscopy), together with many-body Green's function calculations to investigate the spectroscopic and thermodynamic properties of toluene and obtained the IE of the parent ion to be 8.845 eV and the AEs of major fragment ions $C_7H_7^+$, $C_6H_5^+$, $C_5H_5^+$ are measured to be 11.8, 14.4, 16.5 eV, respectively. Especially, the obtained AE of $C_5H_6^+$ was 13.5 eV.

However, as far as we know, there is few theoretical investigations on dissociative photoionization of toluene. In particular, there is very limited information about the geometries of the parent ion and the main fragment ions in the literatures up to date. Moreover, the dissociative photoionization mechanisms of toluene are still unclear so far. Therefore, in the present work, DFT method is employed to investigate the dissocia-

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tive photoionization of toluene. The theoretical IE of toluene, AEs for its fragment ions, transition structures (TS) and intermediates (INT) are determined. The mechanisms of the dissociative photoionization pathways are also discussed on the basis of theoretical and experimental data from literature. In addition, the transition and intermediates states involved in the pathways are also obtained by theoretical calculations and described in detail in this work.

II. QUANTUM CHEMICAL CALCULATIONS

In this theoretical study, all the geometry optimizations of the reactants, transition states, intermediates, and other products are done at the B3LYP level with 6-311++G(d,p) basis sets, and harmonic vibrational frequencies are also computed analytically at the same level in order to characterize the optimized geometries as potential minima or saddle points. The structures of transition states (TS) and intermediates (INT) for dissociative photoionization channels are also identified in this study. To confirm that the obtained transition states connect with the right reactants and products, the intrinsic reaction coordinate (IRC) calculations were performed at B3LYP/6-311++G(d,p) level. On the basis of the obtained stationary points, more accurate energies were then obtained by single-point calculations at the G3B3 level.

The method of G3B3 has been reported elsewhere [15], and only a brief summary is given here. (i) Step 1: produce an initial equilibrium structure at the Hartree-Fock level using the 6-31G(d) basis set. Verify that it is a minimum with a frequency calculation and predict the zero-point energy (ZPE). This quantity is scaled by 0.8929. (ii) Step 2: beginning with the final optimized structure from step 1, obtain the final equilibrium geometry using the full MP2 method with the 6-31G(d) basis set. This geometry is used for all subsequent calculations. (iii) Step 3: a series of single-point energies calculations are carried out at higher levels of theory. The first higher level calculation is MP4/6-31G(d). This energy is then modified by a series of corrections from additional calculations. (iv) Step 4: the MP4/6-31G(d) energy and four corrections from step 3 are combined in an additive manner along with a spin-orbit correction, ΔE(SO), for atomic species only. (v) Step 5: a "higher level correction" (HLC) is added to take into account remaining deficiencies in the energy calculations: (vi) Step 6: finally, the total energy at 0 K is obtained adding the zero-point energy, obtained from the frequencies of step 1 to the energy. This energy is referred to as the "G3 energy". All calculations above-mentioned are all performed with the Gaussian 03 program.

TABLE I Calculated energies of species (neutral toluene and its cation, products, by-produced fragments, intermediates (INT), transition states (TS)) involved in the photodissociation of toluene at the G3B3 level.

Species	E/Hartree	Species	E/Hartree
C_7H_8	−271.327676	INT8	−270.925546
$C_7H_8^+$	−271.000649	INT9	−270.899633
$C_7H_7^+$(P1a)	−270.418143	INT10	−270.311325
$C_7H_7^+$(P1b)	−270.354396	INT11	−270.247426
$C_7H_7^+$(P1c)	−270.352140	INT12	−270.941202
$C_7H_7^+$(P1d)	−270.348937	INT13	−270.838913
$C_7H_7^+$(P2)	−270.429101	INT14	−270.841854
$C_6H_5^+$(P3)	−231.069695	TS1	−270.940680
$C_5H_6^+$(P4a)	−193.617527	TS2	−270.944569
$C_5H_6^+$(P4b)	−193.555189	TS3	−270.957717
$C_5H_5^+$(P5a)	−192.983623	TS4	−270.922209
$C_5H_5^+$(P5b)	−192.969065	TS5	−270.322057
CH_3	−39.790491	TS6	−270.295260
C_2H_2	−77.275720	TS7	−270.944587
H	−0.499671	TS8	−270.957419
INT1	−270.945723	TS9	−270.922040
INT2	−270.971037	TS10	−270.874846
INT3	−270.972507	TS11	−270.229842
INT4	−270.349537	TS12	−270.246221
INT5	−270.296878	TS13	−270.919016
INT6	−270.986721	TS14	−270.824436
INT7	−270.964878	TS15	−270.835974

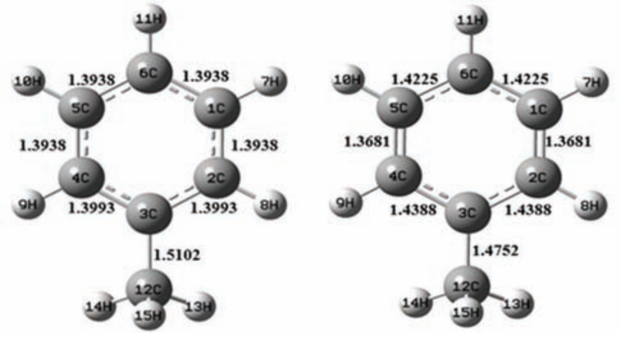
III. RESULTS

With the theoretical calculation, the total energies of species involved in the study of dissociative photoionization of toluene are obtained at the G3B3 level, which are listed in Table I. Especially, the imaginary frequencies of transition states (TS) are given in Tables S3−S17 (see supplementary materials). Because there are lots of different products, intermediates and transition states in the present work, they are named by using their prefix with a unique number, such as P1, INT1 and TS1, which can make them distinguished easily. In the case of isomers, suffixes of a, b, c, *etc.* are applied (for example, P5a) in the dissociative photoionization channel of $C_5H_5^+$.

It is well known that the parent ion $C_7H_8^+$ can be generated directly by a single-photon ionization [10, 14]. The present calculation using G3B3 method gives an adiabatic IE of 8.90 eV, which is in reasonable agreement with the available experimental value, 8.82 eV [10] and 8.845 eV [14]. The IE of C_7H_8 is calculated as follows: $\mathrm{IE}(C_7H_8^+)=E(C_7H_8^+)-E(C_7H_8)=8.90$ eV. In the case of possible dissociation channel $C_7H_8 \rightarrow C_7H_7^+$(P1a)+H, the AE of $C_7H_7^+$(P1a) is obtained from: $\mathrm{AE}(C_7H_7^+(\mathrm{P1a}))=E(C_7H_7^+(\mathrm{P1a}))+E(\mathrm{H})-E(C_7H_8)=$ 11.15 eV, which is in good agreement with the exper-

TABLE II Theoretical and literature values of the ionization energy (IE), appearance energy (AE), and dissociation energy (E_d, theoretical) of possible dissociative photoionization channels.

Ions	IE or AE/eV		Possible dissociation channel	E_d(this work)/eV
	This work	Literature		
$C_7H_8{}^+$	8.90	8.82 [10]		
$C_7H_7{}^+$	11.15(P1a)	11.1±0.1 [12]	$C_7H_7{}^+$+H	2.25
	11.03(P2)	10.71 [11]		
		10.7±0.1 [13]		2.13
$C_6H_5{}^+$	12.72(P3)	12.72 [16]	$C_6H_5{}^+$+CH_3	3.82
$C_5H_6{}^+$	12.32(P4a)	13.50 [14]	$C_5H_6{}^+$+C_2H_2	3.42
	13.69(P4b)			4.79
$C_5H_5{}^+$	15.47(P5a)	16.4±0.2 [30]	$C_5H_5{}^+$+C_2H_2+H	6.57
	16.28(P5b)			7.38



C_7H_8 $C_7H_8{}^+$

FIG. 1 The optimized geometries of the neutral toluene and its cation. (a) C_7H_8, (b) $C_7H_8{}^+$. Bond length is in unit of Å.

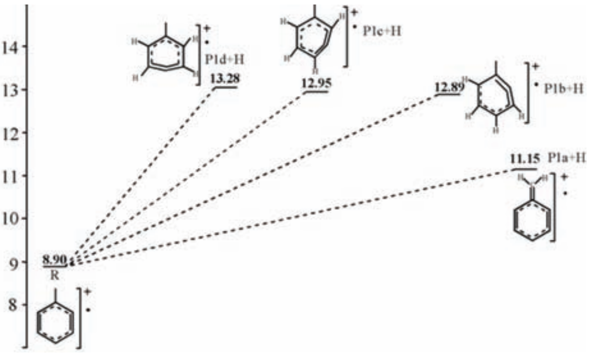


FIG. 2 The dissociation channels for toluene cation to produce fragment ions, $C_7H_7{}^+$(P1) calculated at the G3B3 level. The energy of neutral toluene is defined to be zero.

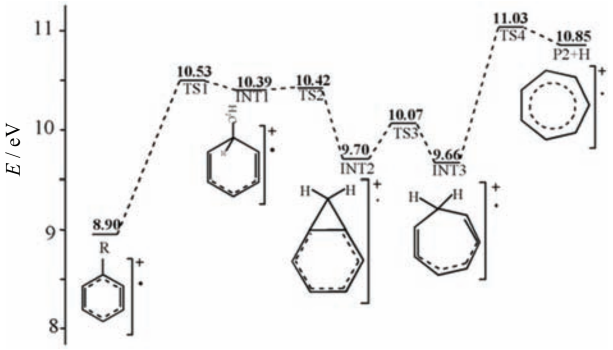


FIG. 3 The dissociation channel for toluene cation to produce fragment ion, $C_7H_7{}^+$(P2) calculated at the G3B3 level. The energy of neutral toluene is defined to be zero.

imental value of 11.1±0.1 eV by Lifshitz *et al.* [12]. As the dissociation energy (E_d) can be calculated by subtracting the IE of parent molecules from the AE of the corresponding fragment ion, the E_d of $C_7H_7{}^+$(P1a) can be expressed in the following form:

$$\begin{aligned} E_\mathrm{d}(\mathrm{C_7H_7^+(P1a)}) &= \mathrm{AE}(\mathrm{C_7H_7^+(P1a)}) - \mathrm{IE}(\mathrm{C_7H_8^+}) \\ &= 2.25\ \mathrm{eV} \end{aligned} \tag{1}$$

In addition, the AEs and E_ds of other products are also obtained in the same way, which are listed in Table II.

The optimized geometries of neutral toluene and its parent cation are obtained at the B3LYP/6-311++G(d,p) level, and all their C−C bond lengths are also calculated, which are all shown in the FIG. 1. From FIG. 1, we can know that some C−C bonds of parent cation become shorter, while some others become longer in comparison with those of neutral molecule, which indicates that dissociation of parent cation will undergo different pathways with the photon energy increase.

IV. DISCUSSION

The fragment ions of toluene in the dissociative photoionization have already been discussed elsewhere [10, 12, 16, 17, 18], wherein the main fragmentation channels have been proposed as follows: $C_7H_7{}^+$+H, $C_6H_5{}^+$+CH_3, $C_5H_6{}^+$+C_2H_2, $C_5H_5{}^+$+C_2H_2+H. However, the detailed dissociative photoionization mechanisms of the fragmentation pathways have not been clarified. In this work, the dissociative mechanisms of $C_7H_8{}^+$ are discussed based on our theoretical results and available experimental data [10−30]. These disso-

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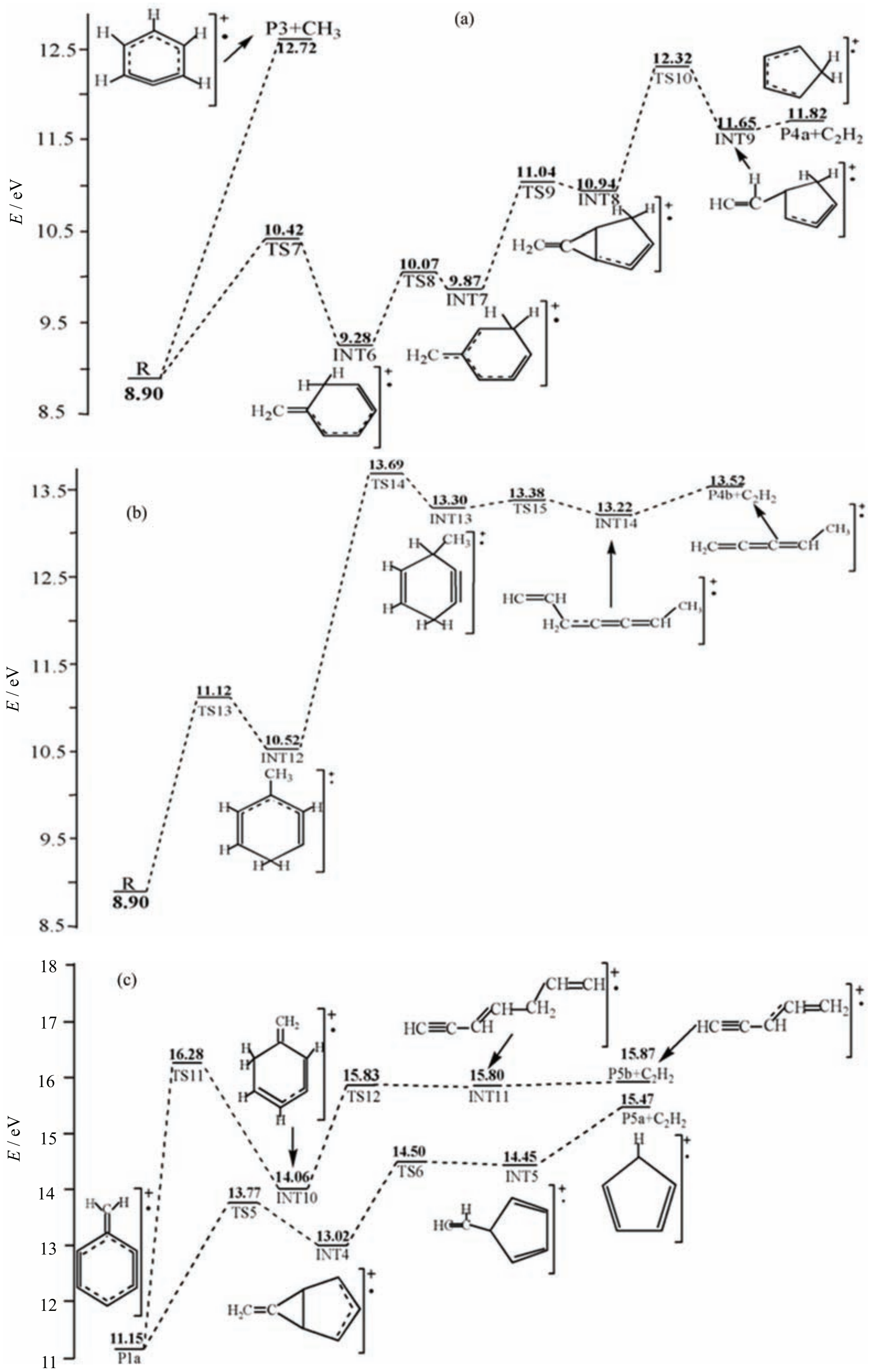

FIG. 4 The dissociation channels for toluene cation to produce fragment ions $C_6H_5^+$(P3) and $C_5H_6^+$(P4a), $C_5H_6^+$(P4b) and $C_5H_5^+$, calculated at the G3B3 level. The energy of neutral toluene is defined to be zero.

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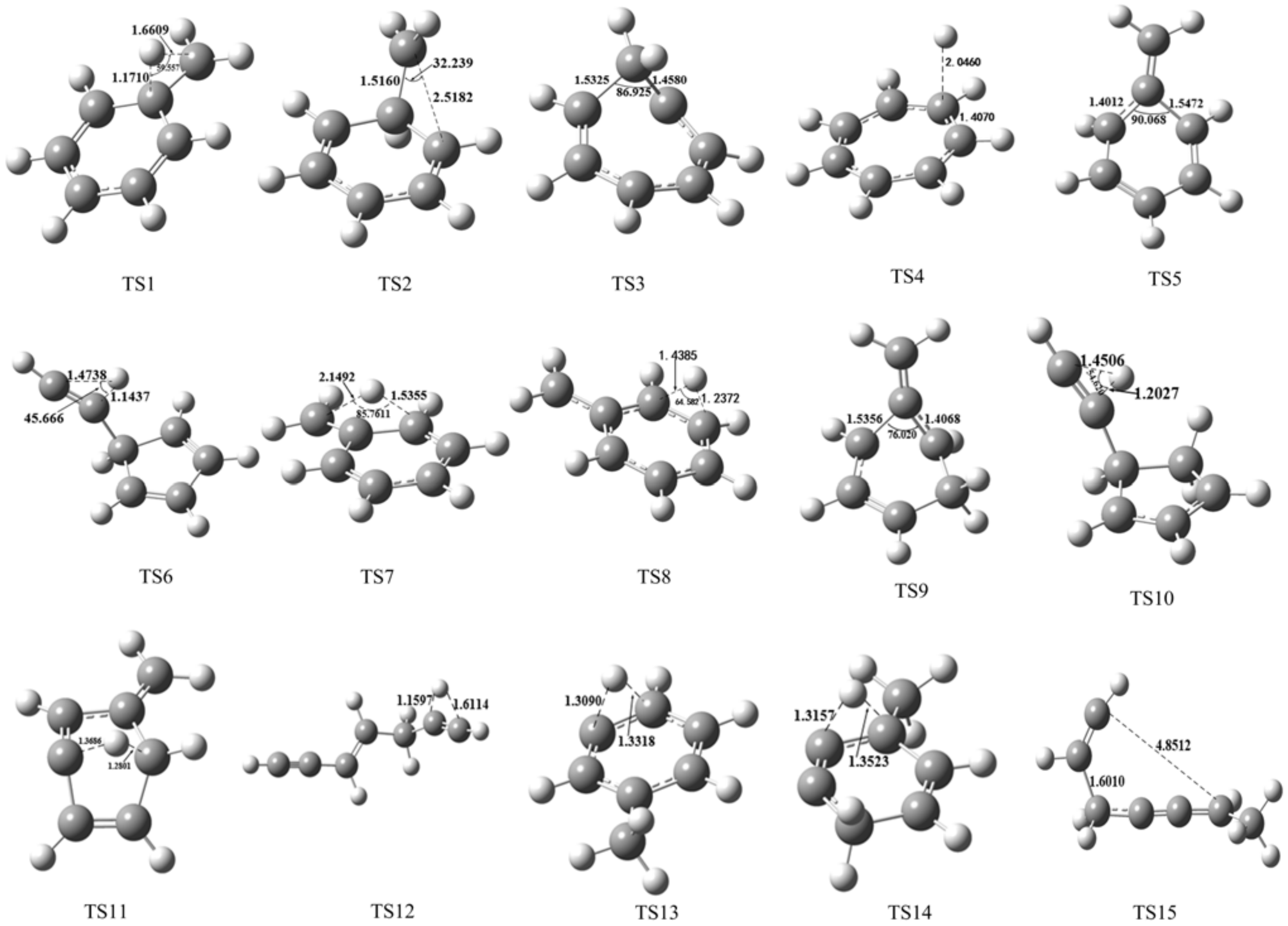

FIG. 5 The geometries of the transition states at the B3LYP/6-311++G(d,p) level. Bond length is in unit of Å and bond angel in unit of (°).

ciative photoionization channels are shown in FIG. 2−4, respectively. In addition, the detailed information on the geometries of the optimized reactants, transition states, intermediates and products are also shown in FIG. 5−7, where the main bond angles and distances are indicated.

As the photon energy increases, the parent ion will undergo different dissociative photoionization pathways. Generally, there are two types of mechanisms for dissociation: direct simple bond cleavage or indirect bond cleavage via transition states and intermediates. For instance, the $C_6H_5{}^+$ ion are formed by loss of CH_3 from the parent ion ($C_7H_8{}^+$). This is one-step dissociation process with no distinct transition states as reported previously [19]. AE of the $C_6H_5{}^+$ ion is predicted to be 12.72 eV, which is in good agreement with available theoretical value (12.72 eV) [16]. By comparing with the structure of parent cation and neutral molecule (see FIG. 1), we found that the C3−C12 and C2−C1 bond lengths are increased by about 0.0350 and 0.0257 Å, respectively, while the C2−C3 and C5−C6 bond lengths are decreased by about 0.0395 and 0.0287 Å, respectively. Especially, the C3−C12 bond is the longest in the parent ion. Therefore, excited by higher photon energy, the C3−C12 bond can be cleaved easily and dissociated to form $C_6H_5{}^+$+CH_3, which agrees with the results in Ref.[14].

A. $C_7H_7{}^+$+H

The structure of $C_7H_7{}^+$ ion has been investigated by various methods [20−22]. Two important isomers of $C_7H_7{}^+$: benzyl (six-membered ring) and tropylium cation (seven-membered ring), are the most important dissociation products of parent ion ($C_7H_8{}^+$) near the threshold [12, 18, 23, 24]. Therefore, there are two possible formation pathways which can produce $C_7H_7{}^+$+H (shown in FIG. 2 and 3).

The benzyl ion is formed by direct loss of H from the parent ion. It is obvious that there are four types of hydrogen atoms in the parent ion. We calculated the AEs of four possible fragment ion isomers, and the outcomes are shown in Table I and FIG. 2.

P1a (($C_7H_7{}^+$) in Table I) is formed from the cleavage of C12−H15 bond, which is 1.1064 Å in length. The

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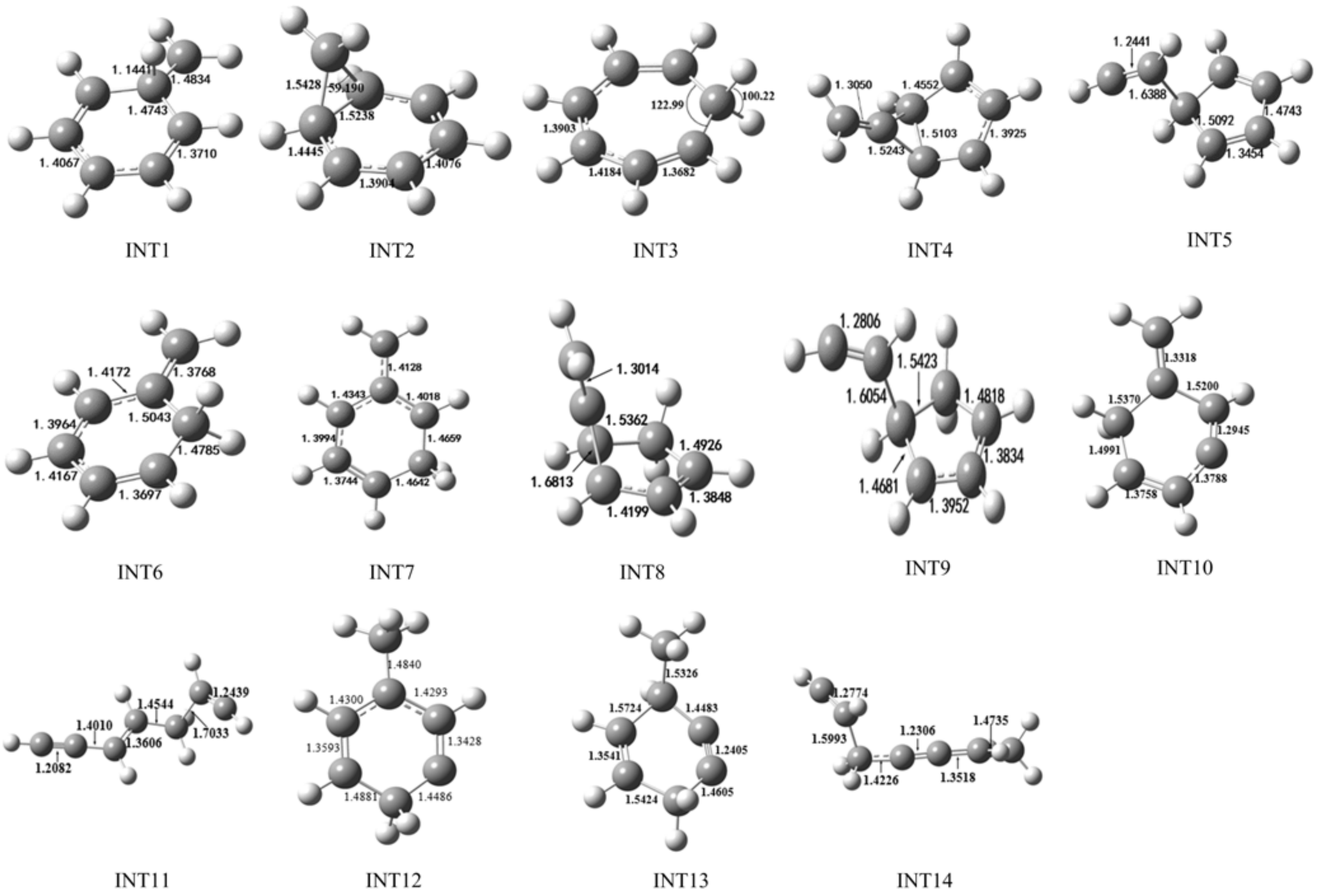

FIG. 6 The geometries of the reactant intermediates at the B3LYP/6-311++G(d,p) level. Bond length is in unit of Å and bond angel in unit of (°).

other three isomers are the H elimination from C1 for P1b, C2 for P1c and C6 for P1d. These C−H bond lengths are 1.0831, 1.0838 and 1.0847 Å correspondingly. And the theoretical AEs for P1a, P1b, P1c and P1d are 11.15, 12.89, 12.95, and 13.04 eV, respectively. It is not surprising to find that the P1a channel is the lowest energy required. There are also possible TS for the other three channels, but their AEs are apparently much higher than the experimental value (11.1±0.1 eV) [12]. Owing to the former theoretical result is in good accordance with the experimental value, 11.1±0.1 eV [12], we tend to consider the H eliminates from the C12. The geometry of the fragment ion P1a at the B3LYP/6-311++G(d,p) level is shown in FIG. 7.

The process for Tropylium cation (seven-membered ring, P2) is somewhat complicated, which need to be carried out via TS and INT, as shown in FIG. 3. Firstly, the hydrogen atom H15 of the methyl group is transferred to the C3 of the benzene ring to form INT1 via TS1. Then, because of the steric effect [29] from the ortho C4 of benzene ring, C12−C4 bond reconstructs to form INT2. Thirdly, INT3 is formed through C3−C2 bond cleavage via TS3. Finally, the INT3 tends to produce P2 by further loss of the H radical via TS4. Calculated AE of this channel is 11.03 eV, which is also in agreement with available experimental value (11.1±0.1 eV) [12].

B. $C_5H_6^+$+C_2H_2

Further dissociation of $C_7H_8^+$ can produce $C_5H_6^+$ and C_2H_2 when the photon energy rises [14, 25]. Flammang and Meyrant *et al.* [25] have studied the structures of gas phase $C_5H_6^+$ ions, which are generated by direct electron ionization of C_5H_6 isomers or dissociative ionization of other precursor molecules (phenol, thiophenol and so on). They have concluded the geometry of $C_5H_6^+$ ion can be identified as the ring structure (P4a), which are from phenol and thiophenol.

Similarly, the geometry of $C_5H_6^+$ ion from $C_7H_8^+$ can also be firstly proposed as the ring structure (P4a), which is shown in FIG. 7. The detailed formation pathway of $C_5H_6^+$ with potential energy is depicted in FIG. 4 (a) and (b). For the ring structure of $C_5H_6^+$(P4a), the decomposition reaction is initiated by methyl H-migration to an ortho carbon, followed by the decomposition to $C_5H_6^+$ and C_2H_2 from $C_7H_8^+$. To

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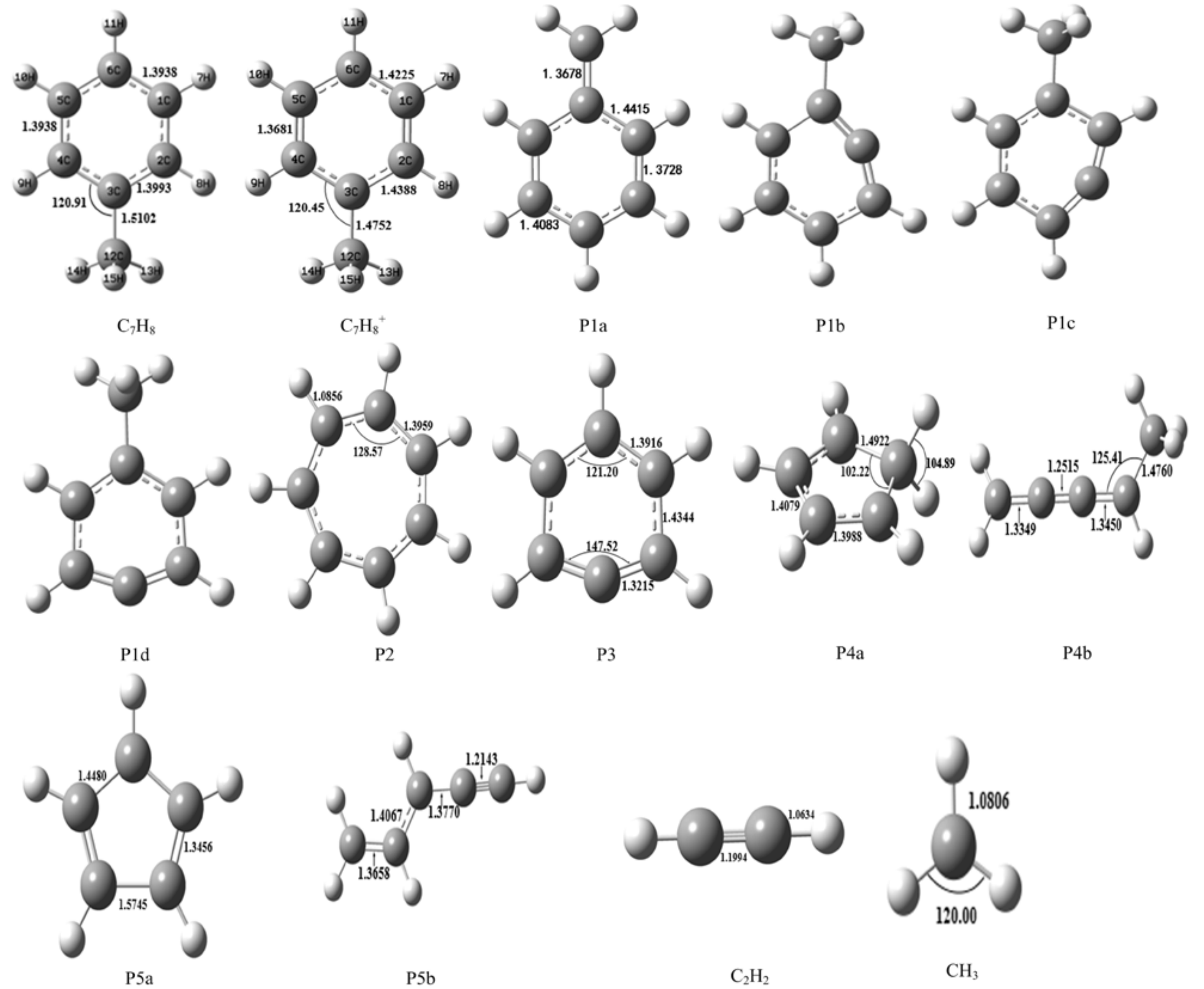

C_7H_8 $C_7H_8{}^+$ P1a P1b P1c

P1d P2 P3 P4a P4b

P5a P5b C_2H_2 CH_3

FIG. 7 The geometries of the neutral toluene, its cation and its fragments (ions and neutrals) at the B3LYP/6-311++G(d,p) level. Bond length is in unit of Å and bond angel in unit of (°).

make it more feasible, the dissociation mechanism is described as follows. (i) First, a TS7 is proposed and the H15 transfers from C12 to C4 with an energy barrier of 1.52 eV, giving rise to INT6. (ii) Second, one H atom on the C4 transfers to C5 via TS8 to produce INT7. (iii) Third, Because of ortho effect, INT8 can be formed via TS9 with an energy barrier of 3.14 eV. Then, one hydrogen atom on C12 is transferred to C3, forming INT9 before C_2H_2 elimination. (iv) Finally, the $C_5H_6{}^+$ is formed by C3−C4 bond cleavage. The theoretical AE in this dissociation pathway is 12.32 eV, which is much lower than the experimental value of 13.50 eV [14]. On the other hand, Li *et al.* [26] has performed experimental and theoretical studies on the dissociative photoionization of *trans*-2-methyl-2-butenal. In their study, the structure of $C_5H_6{}^+$ ion can be identified as chain structure. According to the above situation, the geometry of $C_5H_6{}^+$ ion from $C_7H_8{}^+$ is tentatively identified as the chain structure (P4b) in the present work, which is also shown in FIG. 7. For the chain structure of $C_5H_6{}^+$ (P4b), the calculated AE of $C_5H_6{}^+$ is determined to be 13.69 eV, which is in agreement with the previous value 13.50 eV [14]. FIG. 4(b) shows that the parent cation undergoes a hydrogen atom shift to C6 from C5 to yield the INT12 via TS13. Next, the hydrogen atom migrates from the C4 to its neighboring C3 through TS14 to produce INT13 by overcoming an energy barrier of 3.17 eV. Then, INT14 is formed through C3−C2 bond cleavage via TS15. Finally, $C_5H_6{}^+$(P4b) is yielded with loss of C_2H_2 from INT14, and no barrier for this elimination reaction is found at the B3LYP/6-311++G(d,p) level. The reaction barrier for the formation of $C_5H_6{}^+$ (P4b) is 4.79 eV (relative to parent ion), which is in agreement with the experimental value, 13.50 eV, obtained by Shaw *et al.* [14].

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C. $C_5H_5{}^+$+C_2H_2+H

It is well known that the $C_7H_7{}^+$(P1a) ion produced from parent ion decomposes into $C_5H_5{}^+$ ion by losing C_2H_2 [27]. However, the structure for $C_5H_5{}^+$ is controversial. On the one hand, Occolowitz and White have concluded the geometry of $C_5H_5{}^+$ ion was identified as the chain structure rather than the ring structure by measuring the heat of formation [28]. On the other hand, in the studies on the dissociative photoionization of *p*-nitrotoluene by Zhang *et al.* in 2012, the structure of $C_5H_5{}^+$ ion was identified as ring structure [29].

In this work, both structures are calculated, and we get the TSs and INTs involved in the process using DFT theory. Detailed pathway is described in FIG. 4(c). For the ring structure of $C_5H_5{}^+$(P5a), first, in the benzyl ion (P1a), C2−C4 bond reconstructs via TS5 to form INT4. Next, INT4 undergoes a hydrogen atom shift to C12 from C3 to yield INT5 via TS5. The barrier of this step is calculated to be 1.48 eV. Finally, $C_5H_5{}^+$(P5a) is produced by the fission of C3−C4 bond without any apparent TS. AE of $C_5H_5{}^+$(P5a) obtained from our theoretical (15.47 eV) is much lower than the previous value (16.4±0.2 eV) reported by Tajima *et al.* [30].

For the chain structure of $C_5H_5{}^+$(P5b), the benzyl ion (P1a) undergoes a hydrogen atom shift to C4 from C1 to yield INT10 via TS11. The barrier of this step is calculated to be 5.13 eV. The energies of TS11 and INT10 are higher than that of parent ion by 7.38 and 5.16 eV, respectively. The breaking and forming C−H bond lengths at TS11 are 1.3686 and 1.2801 Å, respectively. Next process is from INT10 to INT11, in which the hydrogen atom migrates from C12 to its neighboring C3 through TS12 by overcoming an energy barrier of 1.77 eV. Finally, P5b is generated by the C3−C4 bond broken in INT11, coupled with a C_2H_2 loss. The overall barrier for the formation of $C_5H_5{}^+$(P5b) is 16.28 eV (relative to neutral toluene), which is in good agreement with the experimental value (16.4±0.2 eV) by Tajima *et al.* [30].

V. CONCLUSION

In this work, quantum chemistry methods have been used to study the photoionization and dissociative photoionization of toluene. The present theoretical results provide several new insights into the dissociative photoionization mechanisms of toluene. The energies and possible dissociative channels for fragment ions from toluene have been estimated on the basis of the quantum chemical calculations. Specific information of fragmentation pathways are discussed in detail. Generally speaking, the dissociative photoionization processes of toluene are somewhat complicated, many of them undergo different dissociative photoionization pathways, such as transition structures, intermediates, H-migration and/or H-elimination, except for the channel ($C_6H_5{}^+$+CH_3), which undergoes direct simple bond cleavage. And some dissociative products have different isomers, which are all distinguished in the present work. In particular, according to calculation and comparison, the $C_5H_5{}^+$ and $C_5H_6{}^+$ can be identified as the chain structure in the dissociative photoionization of toluene. The mechanistic study of dissociative photoionization of toluene will be helpful in understanding the fragmentation.

Supplementary materials: The imaginary frequencies of transition states pertinent to this work are given in Tables S3−S17.

VI. ACKNOWLEDGMENTS

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