Ionization and Dissociation of Benzene and Aniline under Deep Ultraviolet Laser Irradiation

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We report a study on photo-ionization of benzene and aniline with incidental subsequent dissociation by the customized reflection time-of-flight mass spectrometer utilizing a deep ultraviolet 177.3 nm laser. Highly efficient ionization of benzene is observed with a weak C\textsubscript{4}H\textsubscript{3}+ fragment formed by undergoing disproportional C–C bond dissociation. In comparison, a major C\textsubscript{5}H\textsubscript{6}+ fragment and a minor C\textsubscript{6}H\textsubscript{6}+ radical are produced in the ionization of aniline pertaining to the removal of CNH and NH radicals, respectively. First-principles calculation is employed to reveal the photo-dissociation pathways of these two molecules having a structural difference of just an amino group. It is demonstrated that hydrogen atom transfer plays an important role in the cleavage of C–C or C–N bonds in benzene and aniline ions. This study is helpful to understand the underlying mechanisms of chemical bond fracture of benzene ring and related aromatic molecules.

\textbf{Key words:} Photo-dissociation, Mass spectrometry, Benzene, Aniline, Deep ultraviolet laser, C–C bond activation

I. INTRODUCTION

Photon-induced reactions play an important role in modern chemistry and enable researchers to elucidate elementary chemical processes in polyatomic molecules and ions [1], thereby in the past decades extensive efforts have been devoted to both experiments and theoretical studies for illustrating the reaction pathways of polyatomic molecules and cluster ions [1–5], among which the investigations of photo-induced ionization and dissociation mechanisms have attracted considerable interests via mass spectrometry [3–5]. Various ionization methods and mass spectrometry techniques have been developed in recent decades [6–10], which have been used by researchers for customization and personalization of components combined with the general mass spectrometric measurements for chemical identifications. In the ionization process, mass spectrometry in the gas phase can eliminate the uncertainties of ion signals and the contaminating agents and/or impurities from environment [6]. In particular, chemical structures can be determined from fragments analysis by assuming both the mass-to-charge ratio and the precursor/product composition being consistent with each other [11]. The availability of photo-ionization and photo-dissociation in mass spectrometry in identifying chemical structure had important applications in genomics and proteomics [12–14]. Recently, characterizing the photophysical and photochemical properties of small aromatic molecules of benzene (C\textsubscript{6}H\textsubscript{6}) and aniline (C\textsubscript{6}H\textsubscript{7}N), which are also the study samples of this work, has attracted increasing research interest [15, 16].

Benzene is the basic unit of polycyclic aromatic hydrocarbons compounds with each one of all-known six C atoms in a ring attached by an H atom. It is an important precursor molecule to synthesize more complex organic compounds, a natural constituent of crude oil, and an elementary petrochemical [15]. Aniline contains a basic nitrogen atom with a lone pair. It is formally a derivative of ammonia, which is the simplest heteroaromatic molecule, and may be taken as the basic unit for the aromatic amines [16]. Both benzene and aniline are important intermediates in combustion processes [17] and are subjects of many experiments with a variety of techniques, such as multiphoton ionization [18–21], photoelectron-ion coincidence [21], collision-induced dissociation [22], and time-of-flight (TOF) mass spectrometry. Lifshitz et al. [23] reported a study on the photo-dissociation of aniline and predicted that HNC could be a reasonable product.
by measuring the fragment appearance energy. Choe and co-workers [24] proposed a pathway in forming the cyclopentadiene ion and HNC radical. In the photo-dissociation of benzene, Hart et al. [25, 26] studied the possible pathways for the formations of C₆H₅⁺ and C₆H₄⁺ (⁺ refers to ionic radicals). Holland et al. [27] investigated the fragmentation processes occurring in benzene by combining the ion yield curves with the absolute photo-ionization cross-section. However, the photo-dissociation of benzene and aniline in the frequency region of ultraviolet has not yet been studied by a picosecond-pulsed laser at an output wavelength of 177.3 nm, also the C–C/C–N bond activation and the formation pathways of C₆H₅⁺ are still unrevealed and unclear in the photo-dissociation of aniline. Considering that the photo-absorption process of molecules occurs in the femtosecond scale, while the scale of photo-induced structural rearrangement and bond dissociation could be up to nanosecond, ultrashort laser pulses in picosecond may allow for low-fragment mass spectrometric observation prior to molecular structural relaxation [28].

Taking the deep-ultraviolet (DUV) laser (177.3 nm) as an excitation source which possesses advantages in ultrafast ps-pulse (15.5 ps), small pulse energy (~15 µJ), high photon flux (~10¹⁵ photons/s), and high single photon energy (7 eV), we recently have built a reflection time-of-flight mass spectrometer (Re-TOFMS), which has a high resolution and a high sensitivity [29], and proposed a deep-ultraviolet laser ionization mass spectrometry (DUV-LIMS) [30]. In this work, such a mass spectrometer has been used to identify aromatic molecules with minimized structure relaxation and fragmentation. Now, we report a study on the photo-ionization and photo-induced reactions of benzene and aniline by Re-TOFMS, combined with density functional theory (DFT) calculations for full illustration of the experimental findings.

II. EXPERIMENTS AND CALCULATION

A sketch showing the experimental setup of the Re-TOFMS is given in Scheme 1. In the experiment, benzene and aniline molecules in the gas phase were ionized and dissociated by the laser beam at 177.3 nm. The benzene solution was formulated to be a gaseous mixture of 1% benzene with 99% helium according to the saturated vapor pressure [31]. The molecular beam of benzene mixture in helium at pressure 4 atm was expanded into a high vacuum chamber I by the pulsed supersonic process which has a pulse width of ~290 µs duration. While for aniline sampling, 15 µL aniline liquid was dropped into a vacuum tube and was carried into the vacuum chamber I by the supersonic expansion of ~300 µs pulse for helium carrier gas at 5 atm. For both samples of benzene and aniline, the final helium-buffered mixture in the gas phase was collimated with a skimmer, the molecular beam of which was skimmed into the mass spectrometer, and then was ionized and dissociated by the DUV laser beam in the vacuum chamber II. By means of the pulsed acceleration fields, ions in the Re-TOFMS fly vertically to the direction of molecular beam. In addition to the DUV laser ionization mass spectrometry experiments, the mass spectrum with 355 nm laser as ionized light was also obtained as a comparison.

The first-principles calculations were performed with the Gaussian 09 program package [32]. The dissociation pathways of cationic benzene and aniline, the structures of the reactant cations, product cations, potential intermediates, and transition states (TS) were optimized by the B3LYP density functional theory (DFT) [33, 34] with the 6-311++G(d,p) basis set [35, 36]. All of the transition states were checked by a frequency calculation, and the selected transition states were verified with intrinsic reaction coordinate (IRC) [37] calculations to ensure a connection with both sides. Based on the molecular reactions, the reaction pathways were calculated, and the energy of each state was calibrated with zero-point vibrational corrections. Software package of Multiwfn and visual molecular dynamics (VMD) was used for the analysis of natural bond orbital (NBO) donor-acceptor interactions [38, 39]. The profiles of the charge distributions by natural population analysis (NPA) and the all bond lengths are mapped in FIG. S1 in supplementary materials for neutral and cationic benzene and aniline, respectively.

III. RESULTS AND DISCUSSION

FIG. 1 shows the DUV-LIMS observations of photo-ionization and photo-dissociation of gaseous benzene
and aniline. Considering that the ionization energies of benzene and aniline are 9.24 and 7.72 eV, respectively [40, 41], the two molecules undergo two-photon ionization processes at the radiation of 7 eV DUV laser. It is interesting to note that there is a dominant peak at mass-to-charge ratio \(m/z=78\) (C$_6$H$_5$$^+$) corresponding to the parent ion of benzene in FIG. 1(A). In addition, there are a few minor fragment ion peaks appearing at \(m/z=77\) (C$_6$H$_5$H), 63 (C$_6$H$_5$H$^+$), 52 (C$_6$H$_5$$^+$), 51 (C$_5$H$_4$$^+$), 50 (C$_4$H$_3$$^+$), and 39 (C$_3$H$_2$$^+$), respectively. Among them, the peak-to-peak intensity ratios of ions C$_6$H$_5$$^+$ and C$_5$H$_4$$^+$ to their parent are 2% and 1.2%, respectively, indicating dehydrogenation (the potential scanning details please see FIG. S3(a) in the supplementary materials) and C–C bond cleavage. The small peak-to-peak intensity ratios of fragment ions to their parent ions indicate a high ionization efficiency of benzene.

Interestingly, from a dominant parent ion (C$_6$H$_5$N$^+$) of aniline shown in FIG. 1(B), it can be seen that its peak-to-peak intensity ratio reaches as high as 62%, indicating a strong fragment peak, the transfer of hydrogen atom in amino group, and the cleavage/re-bonding of the C–C bond. The benzene ring opens and recloses to a five-membered ring that a C$_5$H$_4$$^+$ fragment is produced and a CNH$^+$ (refers to neutral radicals) tri-atomic radical is removed. Such a ratio is 14% for the ion C$_6$H$_5$N$^+$ at \(m/z=92\), showing a remarkable dehydrogenation (the potential scanning in FIG. S3(b) in supplementary materials). Also, it is worth noting that, the observed molecule ion peak intensity of benzene is 500 times larger than that of aniline. This is partly due to the difference of sampling methods resulting in differently final sample concentrations, as benzene supports the direct vaporizing gas seeded in He gas, while the aniline gas is produced via a bubbling method. Meanwhile, the previously published study showed that benzene bears long-lived excited electronic states (>10 μs) [42], which largely increase the possibility of multi-photon processes under laser radiation (details in FIG. S2 in supplementary materials). It is worth mentioning that the normal 532 nm laser [43] or 355-nm UV laser gives rise to bad fragmentation even at weak laser power density as shown in FIG. 1(C). In this point, the ps-pulsed DUV-LIMS takes advantages to ionize benzene and even its clusters [30, 44], with a significant two-photon ionization process.

Moreover, we have carried out the DFT calculation to explain the cleavage processes of the cationic benzene and aniline. FIG. 2 shows the reaction coordinates initiated by the hydrogen atom transfer (HAT) in the photo-induced dissociations of C–C bond in benzene, where the step-by-step reaction processes are displayed pertaining to the C–C bond cleavage of cationic benzene in forming the fragment ions of C$_6$H$_4$$^+$, C$_5$H$_3$$^+$, and C$_5$H$_2$$^+$, respectively. The favorable channels are found to start from H atom migration along the aromatic ring, followed by ring opening or deforming and then by the C–C skeleton dissociation. Benzene even experiences two hydrogen transfer processes from cationic benzene to state I2a to render the ring opening. Subsequently, there are two competitive pathways between states TS3a and TS3c which produce the three small amounts of fragment ions of C$_4$H$_4$$^+$, C$_4$H$_3$$^+$, and C$_4$H$_2$$^+$, as shown in FIG. 1(A) by a 40 times amplified inset. In addition, the pathway of TS3a→I3a is preferred by more benzene molecule ions due to lower state barrier energies than those in TS3k→I3d.

The alternative HAT process can, along with the removal of a C$_3$H$_3$ or CH$_3$ radical, promote the consecutive ring opening and re-closing to form a stable five-membered ring of benzene cation of C$_5$H$_3$$^+$ or C$_5$H$_4$$^+$ product, where the formation of C$_5$H$_3$$^+$ by a loss of CH$_3$ can compete with the formation of the C$_5$H$_2$$^+$ by loss of C$_3$H$_3$ at high energy. The C$_5$H$_3$$^+$ fragment ions can be regarded as the cyclopropenyl cations with a linear CH$_2$CCH structure of the radical fragment [26]. Two pathways have been found to form a five-membered ring of C$_6$H$_5$$^+$. Specifically, by undergoing a hydrogen transfer process, the cationic benzene can reach a lower state TS1 with a barrier height about 2.12 eV. Thereby, state TS2b could be formed after the ring opening with cleavage of a C–C bond. When the five-membered ring is closed in state I2b by the formation of C–C bond, the alternative hydrogen transfer process in state TS3d competes with the alternative C–C bond cleavage in state TS3b at a high energy.
FIG. 2 Hydrogen transfer processes and C–C bond cleavages of cationic benzene in productions of the fragment ions \( \text{C}_3\text{H}_2^+ \), \( \text{C}_4\text{H}_4^+ \), \( \text{C}_4\text{H}_3^+ \), \( \text{C}_4\text{H}_2^+ \), and \( \text{C}_5\text{H}_3^+ \). The energy (in eV) of cationic benzene, reaction intermediates (Is), transition states (TSs), and products (Ps) is the sum of electronic and zero-point energies. The unit of the bond length is in Å.

FIG. 3 (A) Hydrogen transfer process accompanied with consecutive ring opening and re-closing to form a five-membered ring of aniline cation of ion \( \text{C}_5\text{H}_6^+ \). (B) The proposed hydrogen transfer processes and C–N bond cleavage of cationic aniline in producing the fragment ion \( \text{C}_6\text{H}_6^+ \). The energies (in eV) of cationic aniline, reaction intermediates (Is), transition states (TSs), and products (Ps) are the sum of electronic and zero-point energies. The unit of the bond length is in Å.

Furthermore, FIG. 3(A) depicts the HAT processes in producing the fragment of ion \( \text{C}_5\text{H}_6^+ \) followed by consecutive ring opening and re-closure to form a five-membered ring of cationic aniline. One can see that a hydrogen in the amino group transfers to the benzene ring in the state TS1 with a barrier height of about 3.33 eV, and then turns to state I1 with a lower barrier height of 1.89 eV, which reduces the interaction between two carbon atoms and promotes the relative C–C bond elongation. Thereby, six-membered carbon ring opens in state I2. When the five-membered ring is closed by the formation of C–C bond, the CNH radical is ejected from the ring and forms the \( \text{C}_5\text{H}_6^+ \) in state P. As also depicted in FIG. S5 in supplementary materials, the potential energy threshold value of C–C bond cleavage is about 2.13 eV. Thus, our current observation confirms the similar observations for aniline reported previously [22, 25], while our calculation results well explain the underlying mechanisms of these experimental findings.

FIG. 3(B) shows two tentative hydrogen transfer processes in amino group, accompanied with the cleavage of C–N bond in cationic aniline forming the fragment ion \( \text{C}_6\text{H}_6^+ \). We found that the alternative hydrogen transfer process contributes to the cleavage of C–N bond, giving rise to \( \text{C}_6\text{H}_6^+ \) product along with the removal of an NH radical. There are two possible pathways for an H atom to be transferred from the amino group to the benzene ring. The H atom could be transferred from the amino group and be linked to the neighboring C atom in a reaction state with an energy of 3.33 eV.

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In comparison, there is a slightly larger transition state with potential of 3.40 eV by transferring the H atom from the amino group to the C atom that is linked to the amino group. However, the energy difference between states I1 and P1 is smaller than that between states I2 and P2, as shown in FIG. S6 in supplementary materials, it comes to be less endothermic energy of 3.62 eV to break the C–N bond. Therefore, the $C_6H_6^+$ product exists in the form of benzene cation in the photo-dissociation process of aniline.

Although the photo-induced dissociation of both molecule ions starts from the HAT, aniline differs from benzene in that HAT on amino group expedites fragmentation. In benzene, the HAT on benzene ring increases C–C bond lengths giving rise to disruption of benzene; while in aniline, two modes of the HAT from amino group enlarge the C–C and C–N bond lengths, which contributes to the removal of CNH and NH radicals. In specific, the C–C bond length is enlarged from 1.434 Å of cationic aniline to 1.504 Å of state A-I1 (I1 in FIG. 3(A)), which is contrast to the C–N bond length increased from 1.335 Å to 1.441 Å of state B-II (II in in FIG. 3(B)).

In order to understand the C–C and C–N bond activations of aniline in depth, the natural bonding orbital (NBO) analysis of the second-order perturbative energies ($E(2)$) have been performed to study the interaction mechanisms relating to C3 atom and its adjacent C2 or N atom, before and after ionization, and after H atom transfer (more details in FIG. S7). As shown in FIG. 4(A), the donor-acceptor charge transfer interactions of $BD_{C1-C2} \rightarrow BD_{C3-N}^{*}$ are weaker for C2–C3 bond in the cationic aniline and intermediate of A-I1 ($E(2) = 1.69$ kcal/mol and $E(2) = 1.17$ kcal/mol) than that in neutral aniline ($E(2) = 4.02$ kcal/mol), respectively, indicating that ionization and H atom transfer promote the dissociation of C2–C3 bond and the removal of CNH radical. Also, FIG. 4(B) shows the donor-acceptor charge transfer interactions of $LP_{N} \rightarrow BD_{C2-C3}^{*}$ are weaker in the cationic aniline and intermediate of B-I1 ($E(2) = 19.82$ kcal/mol and $E(2) = 0.35$ kcal/mol) than that in neutral aniline ($E(2) = 25.86$ kcal/mol). And the dominant interaction between C3 atom and N atom is weaker ($E(2) = 5.43$ kcal/mol for $LP_{N} \rightarrow BD_{C3-H14}$, see FIG. S7 in supplementary materials) in the B-I1 than that in the intermediate of B-I2 ($E(2) = 6.14$ kcal/mol for $LP_{N} \rightarrow BD_{C3-C4}$). This again is consistent with the fact that transferring the H from the amino group and linking to the neighboring C encourage the C–N bond to break.

**IV. CONCLUSION**

Utilizing the newly-developed DUV laser ionization mass spectrometry (DUV-LIMS), we have studied the photo-ionization and photo-dissociation process of benzene and aniline molecules. It is found that, besides the dominant peaks of their parent ions, aniline and benzene exhibit largely different photo-dissociation processes. The DFT calculation results have well revealed...
the photo-induced reaction pathways in forming the varied fragment ions. The HAT process was accompanied with asymmetric C–C bond dissociation leading to the production of a minor C₄H₄⁺ fragment in benzene. In contrast, the HAT process facilitates the cleavage of C–N bond, which forms the product of benzene ion along with the removal of an NH radical in aniline. From the dominant dissociation process of aniline, it is more interestingly found that a hydrogen atom transfers from the amino group to the ring, which is accompanied by benzene ring opening and followed by forming a five-membered ring and simultaneously excluding a CNH radical. Detailed reaction coordinates and NBO analysis have well depicted the underlying mechanisms of C–C/C–N bond activations of small aromatic molecules of benzene and aniline. The experiment facts show the high potential of using the Re-TOFMS for studying other similar aromatic molecules and our results provide reliable data for understanding the underlying mechanisms of C–C/C–N bond activation of these aromatic molecules.

Supplementary materials: NPA charge, bond lengths, energetics, thermodynamics, potential energy scan of bond cleavage, and natural bond orbital analysis are shown.

V. ACKNOWLEDGMENTS

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