

Roaming-Mediated CH₂NH Elimination from the Ionization of Aromatic Ethylamines

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The ionization of aromatic ethylamines by photons or electrons leads to elimination of CH₂NH fragments, supposedly deriving from the McLafferty rearrangement involving intramolecular γ -hydrogen transfer. Using tryptamine and phenethylamine as examples, the results reported here suggest that the McLafferty mechanism is inadequate for interpreting the observations of CH₂NH elimination due to much higher calculated appearance energy than experimentally measured values. Furthermore, by considering the roaming-mediated effect, the calculated appearance energy for the elimination of CH₂NH fragments is reduced and matches well with the experimental re-

sults and verifies the existence of roaming-mediated effect. This effect could potentially be extended to explain the general CH₂NH elimination of aromatic ethylamines. Due to the similar hydrogen transfer to that of the McLafferty mechanism, the roaming-mediated effect was taken into account to suggest a novel mechanism, termed the "roaming-modified McLafferty rearrangement", that explains the observations of CH₂NH elimination in the ionization of aromatic ethylamines. This is a reasonable modification of the McLafferty rearrangement mechanism.

1. Introduction

The McLafferty rearrangement is an extensively reported fragmentation reaction in mass spectrometry for cations bearing a diverse range of functional groups. It involves γ -hydrogen transfer through a six-membered transition state before cleavage of the α - β bond.^[1] This type of reaction was reported for electron impact (EI) ionization of aliphatic acids with the formation of a vinyl group in 1952.^[2] More evidence for this rearrangement reaction was found with the decomposition of ionized aliphatic aldehydes, ketones, esters, amides and other derivatives with observation of elimination of vinyl hydrocarbons.^[3-7] The origin of γ -hydrogen transfer has been established by extensive experiments involving deuterium and heavy-atom labeling.^[8-10] McLafferty proposed the electronic mechanism for this type of rearrangement reaction,^[11,12] involv-

ing γ -hydrogen transfer. This type of reaction was named after him and has been reported generally for other chemical systems.^[13-20]

Aromatic ethylamines are fundamental chemical materials and include phenethylamine-derived neurotransmitters.^[21] Due to their importance, extensive research has been carried out on their photochemical and decomposition properties.^[22-24] Resonance-enhanced multiphoton ionization and vacuum ultraviolet (VUV) photoionization of aromatic ethylamines lead to two decomposition channels,^[23,24] involving the elimination of the neutral CH₂NH fragment (-29 Da) and the formation of CH₂NH₂⁺ (*m/z* 30), respectively (Figure 1). The universal CH₂NH

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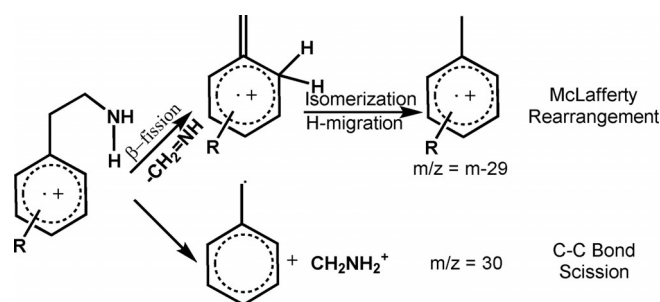


Figure 1. The decomposition channels of aromatic ethylamine radical cations.

elimination pathway has been previously proposed to arise from γ -hydrogen transfer by the McLafferty rearrangement.^[23,24] To test this, ab initio calculations have been performed.^[23] However, it was found the calculated appearance energies (AEs) for the McLafferty mechanism were higher than

experimental observations by approximately 1.0 eV, indicating that this mechanism is not plausible for explaining the experimental results, which motivated us to conduct this study.

The roaming mechanism has been newly reported as a peculiar reaction pathway that bypasses the conventional saddle-point transition state entirely.^[25,26] It has been clearly demonstrated in several chemical reactions,^[26–30] and furthermore is now assumed to be somewhat general.^[31,32] It was validated in the photodissociation of formaldehyde for the first time, involving hydrogen “atom roaming” over a long range before bonding with the other hydrogen atom, to give the closed-shell products of H₂ and CO, with the H₂ formed with extremely high vibrational excitation.^[26] Subsequently, the “radical roaming” pathways were reported for the photodissociation processes of acetaldehyde and in other chemical systems.^[29,30,33–35] The roaming radical mechanisms derived from the near-dissociation of a C–C bond^[33,35] suggest that similar roaming reactions could exist in the photochemistry of aromatic ethylamines. Because the C_α–C_β bond in aromatic ethylamine cations is weak, we anticipated seeing whether the CH₂NH₂ radical roaming mechanism governs CH₂NH elimination, involving γ -hydrogen atom transfer.

In this study, we utilized synchrotron-based VUV photoionization mass spectrometry (SVUV PI MS) combined with ab initio calculations to search for evidence for a roaming-mediated mechanism in the photoionization of aromatic ethylamines, taking tryptamine and phenethylamine as examples. Due to the similar chemical properties of these two molecules, the reaction mechanisms corresponding to their decomposition could be extended to a number of aromatic ethylamines. The photoionization of the two molecules with SVUV light involves a single-photon ionization process.^[36–39] Additionally, the photoionization efficiency (PIE) curves of the generated ions were measured by tuning the photon energy continuously. According to the PIEs, the ionization energies (IEs) and AEs for dominant fragment ions were determined.^[36,38] The diagnostic AE values are key for discriminating the possible decomposition mechanisms.^[38,40] Theoretical calculations were used to investigate in some detail the proposed roaming-mediated CH₂NH elimination from tryptamine and phenethylamine cations.

2. Results and Discussion

Typical VUV photoionization mass spectra of tryptamine and phenethylamine are shown in Figure 2. The photoionization of these two molecules is a single-photon ionization process.^[30] Only molecular ions at m/z 160 and 121 were observed at photon energies of 7.60 (Figure 2a) and 7.50 eV (Figure 2c), respectively, arising from near-threshold photoionization. The observed ion signals of m/z 131 at 8.50 eV (Figure 2b) and m/z 92 at 11.00 eV (Figure 2d) derive from the elimination of closed-shell CH₂NH fragments, which were confirmed by the EI/HR-TOF MS. The signal of m/z 30 assigned to CH₂NH₂⁺ was not observed in the spectrum shown in Figure 2b, because the formation of CH₂NH₂⁺ in the ionization of tryptamine requires much higher photon energy than that of m/z 131.^[41] Furthermore, the mass spectrum of phenethylamine at a photon

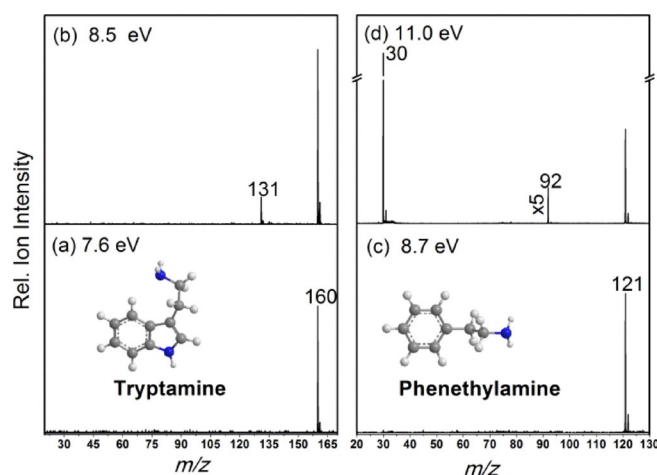


Figure 2. Typical VUV photoionization mass spectra of tryptamine (a and b) and phenethylamine (c and d) at different photon energies.

energy of 11.0 eV shows a highly intense signal of m/z 30 (CH₂NH₂⁺), arising from direct C_α–C_β bond scission.

Figure 3 shows the PIE curves of ions upon changing the

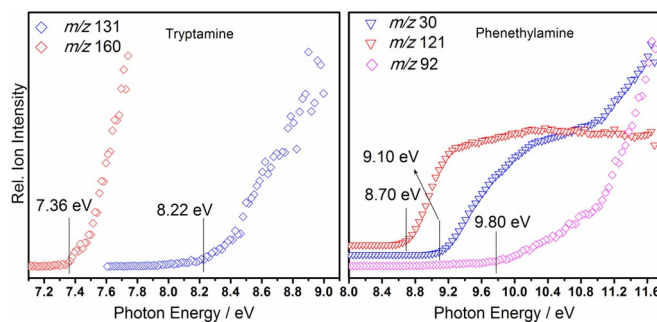


Figure 3. The photoionization efficiency (PIE) curves for ions generated in the ionization of tryptamine and phenethylamine. The curves were obtained by integrating the area of each mass peak versus photon energy.

photon energy continuously, based on which the adiabatic IEs of tryptamine and phenethylamine molecules were determined to be approximately 7.36 and 8.70 eV within the uncertainty of ± 0.05 eV, respectively. Also, the ion signals of m/z 131, 92 and 30 exhibit sharp increases at approximately 8.22, 9.80 and 9.10 eV, which are assessed to be the AEs for C₉H₉N⁺, C₇H₈⁺ and CH₂NH₂⁺, respectively. These signals are diagnostic for the different possible decomposition mechanisms.^[1] Comparatively, the IE/AE values calculated with the G3B3 method^[42] are in accordance with the measured values, as listed in Table 1. The error in the calculated results is about 0.3 eV. Domelsmith et al. reported IE values for tryptamine and phenethylamine of 7.69 and 8.50 eV,^[22] respectively, which are close to the measurements in this work.

Typically the aromatic ethylamine radical cations were proposed to undergo CH₂NH elimination to generate a McLafferty-type ion [M–CH₂NH]⁺ and CH₂NH₂⁺ formation through C_α–C_β bond breaking upon photon excitation.^[1] We used the theoretical calculations of potential energy surfaces (PESs) at the

Table 1. The experimentally measured and calculated IE/AE values in this work.							
	<i>m/z</i>	Formula	IE/AE ^[a] [eV]	Ref. [eV] ^[b]	Calcd [eV] ^[c]	Neutral loss	Mechanism
Tryptamine	160	C ₁₀ H ₁₂ N ₂ ⁺⁺	7.36	7.69	7.33	–	–
	131	C ₉ H ₉ N ⁺⁺	8.22	–	8.33	CH ₂ NH	roaming
					9.36		McLafferty
Phenethylamine	121	C ₈ H ₁₁ N ⁺⁺	8.70	8.50	8.59	–	–
	92	C ₇ H ₈ ⁺⁺	9.80	–	9.66	CH ₂ NH	roaming
	30	CH ₂ NH ₂ ⁺	9.10	–	10.40 9.36	–	McLafferty –

[a] Experimental data with an uncertainty of ±0.05 eV. [b] Ref. [19]. [c] Calculated using the G3B3 method.

G3B3 level of theory for this process to clarify the mechanism of CH₂NH elimination in the decomposition of photoionized tryptamine and phenethylamine. Figure 3 displays the calculated stationary points on the PESs for CH₂NH elimination processes in the dissociation of tryptamine radical cation. Previous works have revealed several conformational isomers of gaseous tryptamine, which could isomerize into each other by overcoming low energy barriers.^[43,44] We used the G3B3 method to optimize the conformers of tryptamine and select one representative, named RC1, to investigate its decomposition pathways. The energy of ground-state RC1 was taken as zero, and the ionization energy for RC1 was calculated to be 7.33 eV, which is close to the experimental value of 7.36 eV, indicating that the G3B3 method provides a sufficiently high computational accuracy.

The typical McLafferty rearrangement mechanism is outlined in Figure 4, and involves intramolecular γ -hydrogen transfer via a six-membered transition state (McL-TS1). The energy barrier for this H-transfer process, calculated by the G3B3 method, is estimated to be approximately 1.75 eV. At higher energy, the length of the C _{α} –C _{β} bond increases greatly to 2.026 Å in McL-TS2, the breaking of which leads to the formation of C₉H₉N⁺⁺ (PC1, *m/z* 131), accompanied by the loss of the CH₂NH fragment. The AE of C₉H₉N⁺⁺ along this pathway was calculated to be 9.36 eV (McL-TS2). However, the diagnostic experimental

value is 8.22 eV, which is lower than the computed value by nearly 1.14 eV, indicating that the McLafferty rearrangement mechanism would be a poor interpretation of the experimental results.

We wondered whether an unknown alternative mechanism to the McLafferty rearrangement was yet to be found for the CH₂NH elimination. Previous studies had suggested the roaming radical mechanism for some cases. Hence, we supposed that the CH₂NH₂ radical roaming-mediated γ -hydrogen transfer mechanism governs the primary CH₂NH elimination, by minimizing the energy barrier in the decomposition of aromatic ethylamine cations. As such, the roaming effect involves the CH₂NH₂ radical rotating to move the γ -hydrogen in the NH₂ group closer to the residual radical during C _{α} –C _{β} bond fission. After the intramolecular hydrogen atom transfer (H shift) from NH–H to C _{α} , the roaming-type ions, namely PC2 and PC4 (see below), are produced in the cases of tryptamine and phenethylamine, respectively.

The calculation of stationary points on the PES for the roaming-mediated CH₂NH elimination was performed at the G3B3 level to provide further insights into the CH₂NH₂ radical roaming pathway (red line in Figure 4). Typically, the length of the C _{α} –C _{β} bond increases markedly to trigger the roaming of the CH₂NH₂ group over a large scale (4.146 Å in Roam-INT1). Furthermore, the CH₂NH₂ group rotates around its C–N bond, leading to the NH₂ group moving close to the C _{α} position. Whereas the γ -H atom in NH₂ group is close enough to the C _{α} atom (1.550 Å in Roam-TS1), the CH₂NH residual fragment is lost, accompanied by the H transfer to C _{α} to give the product PC2 (3-methylindole cation, *m/z* 131). The calculation shows the CH₂NH₂ radical roaming in the region of 3–4 Å.

We calculated the process of breaking the C _{α} –C _{β} bond in the tryptamine cation at the LC-BLYP/6–311G(d,p) level,^[45,46] as shown in Figure 5 a. Our calculation indicates that a dissociation energy of approximately 1.73 eV (40.00 kcal mol^{–1}) is required to directly break the C _{α} –C _{β} bond, accompanied by the loss of a CH₂NH₂ radical. However, the overall energy barrier for the roaming-mediated C _{α} –C _{β} bond fission, which induces CH₂NH elimination, was computed to be 1.16 eV (26.85 kcal mol^{–1}) relative to the RC1⁺. It again suggests the tryptamine cation prefers to undergo the CH₂NH elimination along the proposed roaming mechanism, which fits well with the experimental observation of *m/z* 131 prior to the signal of *m/z* 30.

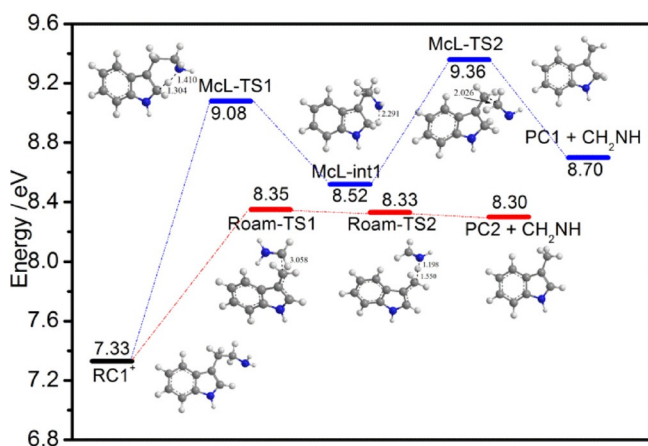


Figure 4. Potential energy surfaces for the ionization–dissociation of tryptamine. Blue line: the representative McLafferty rearrangement pathway; red line: the roaming pathway. The calculation was performed at the G3B3 level.

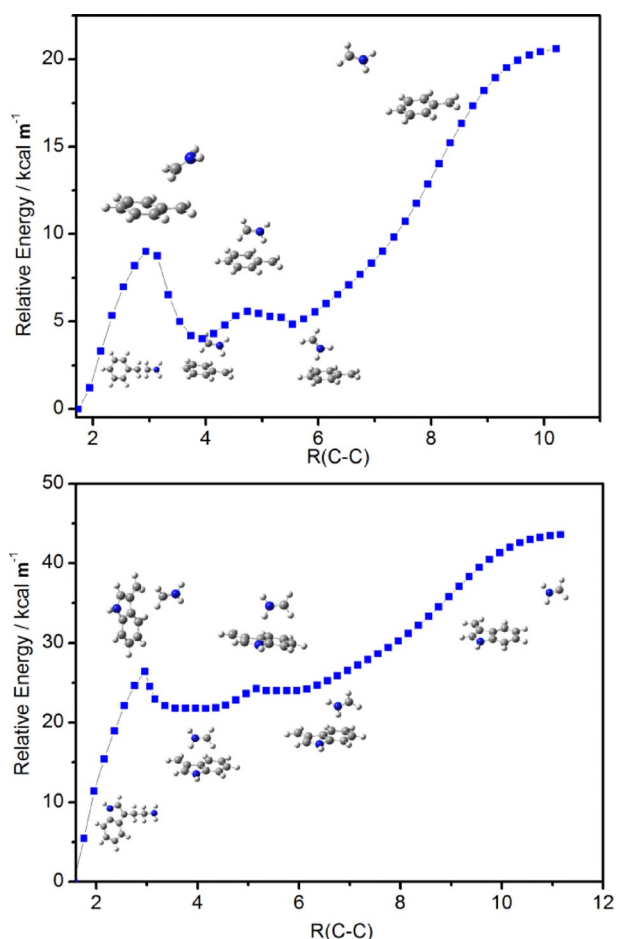


Figure 5. The C_α-C_β bond breaking curves of a) tryptamine and b) phenethylamine cations; bond lengths are expressed in Å. In addition to the direct breaking of the C_α-C_β bond to generate the CH₂NH₂⁺ fragment in the decomposition of tryptamine and phenethylamine cations, the CH₂NH₂ group roams in a large spatial region as the length of C_α-C_β bond increases. The roaming effect brings the NH₂ group closer to C_α. The calculation was performed at the LC-BLYP/6-311G(d,p) level.

The AE of C₉H₉N⁺⁺ in the roaming mechanism was computed to be 8.33 eV, which is in good agreement with the experimental value of 8.22 ± 0.05 eV. However, the AE value from the McLafferty mechanism is estimated to be 9.36 eV, which is much higher than the experimental observation. Conclusively, the roaming-mediated mechanism works well to explain the CH₂NH elimination in the decomposition of tryptamine radical cation.

Previous reports stated that the ionization of aromatic ethylamines excited by photon or electron usually gives the fragment CH₂NH₂⁺ (*m/z* 30) by direct C_α-C_β scission.^[40] In fact, the ionization of tryptamine leads to a weak signal of *m/z* 30 (CH₂NH₂⁺),^[3] not shown in Figure 2. Calculation at the G3B3 level predicts the AE value of CH₂NH₂⁺⁺ to be 9.23 eV, much higher than that of C₉H₉N⁺⁺ in the roaming mechanism. This indicates that the roaming-mediated CH₂NH elimination pathway governs the dissociation of the tryptamine cation.

Furthermore, CH₂NH elimination was also observed in the photoionization of phenethylamine (Figure 2). The IE value was calculated to be 8.59 eV, close to the experimental value of

8.70 eV. Similarly, the McLafferty mechanism was proposed to account for the CH₂NH elimination in the decomposition of the phenethylamine cation. We used the G3B3 method to obtain further insight into the McLafferty mechanism (Figure 6,

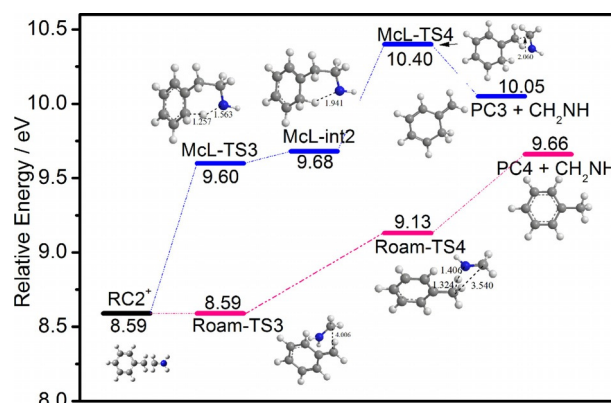


Figure 6. Potential energy surfaces for the ionization-dissociation of phenethylamine. The RC2⁺ represents the phenethylamine cation. Blue line: the McLafferty rearrangement pathway for CH₂NH elimination; red line: the roaming-mediated pathway. The calculation was performed at the G3B3 level.

blue line). The intramolecular γ -hydrogen transfer occurs via the six-membered transition state McL-TS3 and then the C_α-C_β bond cleaves to give C₇H₈⁺⁺ (PC3, *m/z* 92), accompanied by the loss of CH₂NH fragment. The AE for C₇H₈⁺⁺ in this mechanism was computed to be 10.40 eV, which is much higher than the experimentally measured value of 9.80 eV, indicating that the McLafferty mechanism is not the primary dissociation pathway.

As in the case of tryptamine, the mechanism involving roaming is proposed to interpret the observation of CH₂NH elimination in the decomposition of the phenethylamine cation. The calculated results at the G3B3 level are shown in Figure 6 (red line) for the proposed roaming-mediated CH₂NH elimination. As the length of the C_α-C_β bond increases, the C_β atom moves far away from C_α (to a distance of 5.045 Å in Roam-INT2). The CH₂NH₂ radical roams over the long range of 3–5 Å to move the NH₂ group close to C_α, accompanied by the CH₂NH₂ radical rotating around the C–N bond. The γ -H atom in the NH₂ group is transferred to C_α to form PC4 (C₇H₈⁺⁺; *m/z* 92) while it is close enough to C_α (1.311 Å in Roam-TS2), followed by the loss of CH₂NH fragment. The AE for C₇H₈⁺⁺ in this mechanism is computed to be 9.66 eV, close to the experimental value of 9.80 eV. In conclusion, the proposed roaming-mediated mechanism accounts for the observation of CH₂NH elimination in the ionization of phenethylamine.

We also calculated the process of breaking the C_α-C_β bond in the phenethylamine cation (RC2⁺) at the LC-BLYP/6-311G(d,p) level (Figure 5). The increase of the C_α-C_β bond length of the phenethylamine cation leads to two parallel patterns of C_α-C_β bond fission. The process of direct C_α-C_β bond breaking requires energy of approximately 0.65 eV (15 kcal mol⁻¹). Additionally, the overall energy barrier for the roaming-mediated C_α-C_β bond breaking, involving hydrogen transfer

from NH_2 group, was computed to be 0.86 eV (19.78 kcal mol⁻¹) relative to the RC^{2+} . The photoionization of phenethylamine leads to a highly intense signal of m/z 30 assigned to CH_2NH_2^+ (Figure 2d), deriving from the direct fission of $\text{C}_\alpha\text{--C}_\beta$ bond. The computed AE value of 9.36 eV for CH_2NH_2^+ is close to the experimental observation of 9.10 eV (Figure 3). Furthermore, the calculated AE of 9.66 eV for $\text{C}_7\text{H}_8^{+\bullet}$ in the roaming pathway is higher than that of CH_2NH_2^+ , which is in good agreement with the fact that the intensity of the ion at m/z 30 is higher than that of m/z 92 (Figure 3). The decomposition of the phenethylamine cation involves $\text{C}_\alpha\text{--C}_\beta$ bond breaking to generate CH_2NH_2^+ and CH_2NH elimination is accompanied by formation of $\text{C}_7\text{H}_8^{+\bullet}$. The roaming-mediated γ -hydrogen transfer mechanism governs the process of CH_2NH elimination.

Previous research has suggested that the McLafferty rearrangement is responsible for CH_2NH elimination in the ionization of aromatic ethylamines.^[1] Our study suggests that the roaming-mediated γ -hydrogen transfer explains well CH_2NH elimination in the dissociation of tryptamine and phenethylamine cations. Furthermore, this mechanism is believed to be general in the ionization of aromatic ethylamines. Concerning the similar γ -hydrogen transfer in a typical McLafferty rearrangement, we propose the roaming-modified McLafferty mechanism for interpreting the CH_2NH elimination, as depicted in Figure 7, and believe this mechanism more consistent with the observation of CH_2NH elimination than the typical McLafferty pathway under low-energy excitation.

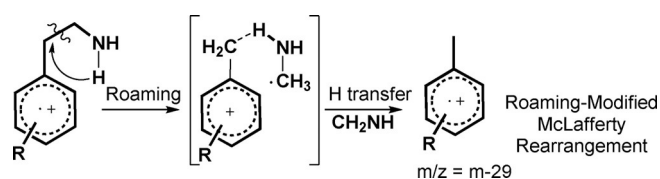


Figure 7. Roaming-modified McLafferty rearrangement for CH_2NH elimination in the ionization of aromatic ethylamines.

3. Conclusions

CH_2NH elimination was observed generally upon the ionization of aromatic ethylamines. Tunable VUV PI MS and theoretical calculations were used to elucidate a possible decomposition mechanism for the elimination of the closed-shell CH_2NH fragment, selecting tryptamine and phenethylamine as representatives. Previous studies have suggested the McLafferty rearrangement regulates the CH_2NH elimination process in the decomposition of aromatic ethylamines. However the present work suggests that a roaming-mediated γ -hydrogen transfer mechanism for CH_2NH elimination fits much better with experimental observations. We term this reaction the “roaming-modified McLafferty mechanism” and believe it is general for the ionization of aromatic ethylamines.

However, further efforts are needed to clarify the excited-state dynamics of aromatic ethylamines to better understand the roaming process. Other experiments, including infrared multiphoton dissociation, state-selective and time-resolved

spectroscopy and ion imaging might be useful for fundamentally understanding the dynamics of the roaming mechanism for ionized aromatic ethylamines and related compounds. This is the first study to report the roaming effect in the decomposition of radical cations. Our results pave the way for probing the nature and dynamics of the roaming mechanism in the dissociation of gaseous ions.

Experimental Section

We utilized tunable SVUV radiation and ab initio methods to perform this study. The experiments were performed at the National Synchrotron Radiation Laboratory (Hefei, China). The detailed description of experimental apparatus has been provided elsewhere.^[47–50] In brief, a monochromator was used to select the VUV light with defined energy from an undulator in an 800 MeV electron storage ring, as the ionization source for the mass spectrometer. A home-made reflection TOF mass spectrometer served as the mass analyzer with microchannel plates as ion detectors. The generated ion currents were recorded and analyzed with a multiscaler.

The gaseous tryptamine molecules were generated by the 1064 nm infrared laser desorption (IR LD) technique with a Nd:YAG laser.^[48] In contrast, the experiments on phenethylamine were performed using a molecular beam facility coupled to SVUV PI MS.^[49] Typically, the sample of phenethylamine was heated to 250 °C to generate the gaseous sample stream in a stainless evaporator. After dilution with argon, the gas mixture stream was introduced into the ionization chamber (10^{-6} Torr) by a molecular beam system.

Computational Methods

The geometric parameters for the stationary points on the dissociation PESs of tryptamine and phenethylamine were optimized at the G3B3 level.^[42] The intrinsic reaction coordinate calculations were used to validate the energy profiles connecting transition states and intermediates with designated reactants and products. We used the LC-BLYP/6-311G(d,p) method to scan the PES for $\text{C}_\alpha\text{--C}_\beta$ bond dissociation processes with 0.2 Å intervals. All calculations were performed with the Gaussian 09 program package.^[51]

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: atom roaming · CH_2NH elimination · ionization · McLafferty mechanism · synchrotron vacuum ultraviolet radiation

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