

Vibrational Spectroscopy of Aniline Cations and their H-loss Cations in Helium Droplets

Arisa Iguchi,^{*,†,‡} Amandeep Singh,[¶] Susumu Kuma,^{*,‡} Hajime Tanuma,[†] and Toshiyuki

Azuma,^{‡,†}

[†]Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

[‡]Atomic, Molecular and Optical Physics Laboratory, RIKEN, Wako, Saitama 351-0198, Japan

[¶]Department of Chemistry, University of Southern California, Los Angeles, California 90089,

United States

E-mail: iguchi-arisa@ed.tmu.ac.jp; susumu.kuma@riken.jp

Abstract

We produced aniline cations ($\text{c-C}_6\text{H}_5\text{-NH}_2^+$) and their dehydro- (H-loss) cations inside helium droplets by electron ionization and observed their mass-selected vibrational spectra in the N–H stretching region. We observed vibrational bands at $m/q = 93$ which were identified as aniline cations. These bands showed only a few cm^{-1} shifts from the symmetric and anti-symmetric N–H stretching bands for the amino ($-\text{NH}_2$) group in the gas phase. For the H-loss cation at mass $m/q = 92$, the agreement of the observed N–H band frequency with the result of DFT calculations suggests several candidate species, including a seven-membered ring structure, 4-monodehydro azepinylium ($\text{c-C}_6\text{NH}_6^+$). A new reaction pathway to this cation was discussed by considering large excess energy in the ionization process.

Introduction

Molecular spectroscopy using superfluid helium nanodroplets ¹ has opened the frontiers of low-temperature molecular science. The droplets provide an ideal homogeneous environment as a matrix and allow free rotation of the molecules owing to the weak perturbation by superfluid helium. ¹ These advantages have been applied to investigate neutral molecules and, nowadays, molecular ions in helium nanodroplets. ² Recently, an efficient, versatile ionization method was demonstrated. ³ The electron ionization of the droplets likely first leads to the formation of He^+ , which is followed by charge transfer to a neutral molecule in the droplet and its subsequent ionization, $\text{M} + \text{He}^+ \rightarrow \text{M}^+ + \text{He}$, where the ionization energy of the embedded molecule (M) is often much smaller than that of He (24.6 eV). The produced cation is immediately cooled to the droplet's intrinsic temperature of 0.4 K. This ionization process produces various cationic species inside the droplet. For instance, when we ionize neutral dimers by this method, the ion-molecule reaction occurs in the droplets. Then, metastable structures as the reaction intermediate can be observed, which are kinetically stable in a helium droplet environment but difficult to realize in the gas phase. Recent observation of the hemibonded water dimer cation ⁴ is good evidence of the advantage of this method, illustrating efficient cooling of the cations produced in the superfluid helium environment.

This study reports the vibrational spectroscopy of aniline cations ($\text{c-C}_6\text{H}_5\text{-NH}_2^+$) in helium droplets prepared by this method. Historically, the aniline cation is the first molecular ion whose vibrational and electronic transitions were reported in helium droplets. ^{5,6} Instead of electron ionization, Drabbels et al. ^{5,6} applied resonant-enhanced multiphoton ionization of the neutral anilines to produce the ions inside the droplets. The ejection mechanism was used to measure the

infrared and visible transitions, where the excited ions are nonthermally ejected from the droplets as bare ions or with several helium atoms. Vilesov and co-authors revisited this ejection process³, where repeated cycles of photon absorption and He evaporation by relaxation explain the production of the bare ions. The ionization processes of aniline in the droplets were studied in more detail by the Kong group.^{7,8}

The infrared spectra of aniline in the gas phase have been well-studied using various methods.^{9–11} The parent and fragment ions have been spectroscopic targets. It is known that the cyclopentadiene radical cation $\epsilon\text{-C}_5\text{H}_6^+$ ($m/q = 66$), which has a five-membered ring frame, forms upon the ionization of aniline. Zeh et al.¹¹ observed the vibrational bands of this cation after ionization, but no intermediates, especially like the short-lived imine tautomer ($\epsilon\text{-C}_6\text{H}_6=\text{NH}^+$) of the aniline cation, were found at the parent mass of $m/q = 93$. Recently, Rap et al.¹² reported the production of the H1- and H2-cyanocyclopentadiene cations (described as 2- or 3-monohydro CPD–CNH⁺ cations in this study) at $m/q = 92$ as H-loss from aniline in the vibrational spectroscopy measured in the range of an infrared free electron laser (550–1800 cm^{-1}), and discussed their relevance to astrochemistry.^{13, 14}

In this study, by employing the electron ionization method, we performed the vibrational spectroscopy of the aniline cation and the H-loss cation in helium droplets in the N–H stretching region. The vibrational excitation was achieved by introducing a tunable IR-OPO/OPA infrared laser, and the resulting bare cationic species were detected employing a time-of-flight (TOF) mass spectrometer. This work reports the first experimental observation of the anti-symmetric N–H stretching band of the aniline cation in addition to the previously reported symmetric stretching band.⁵ The structure of the H-loss cation at $m/q = 92$ was discussed by comparing the observed

band with the results of DFT calculations. Our study suggests, as a possibility among other candidates, the formation of a new seven-membered ring structure which was not previously found in the gas phase.

Experimental

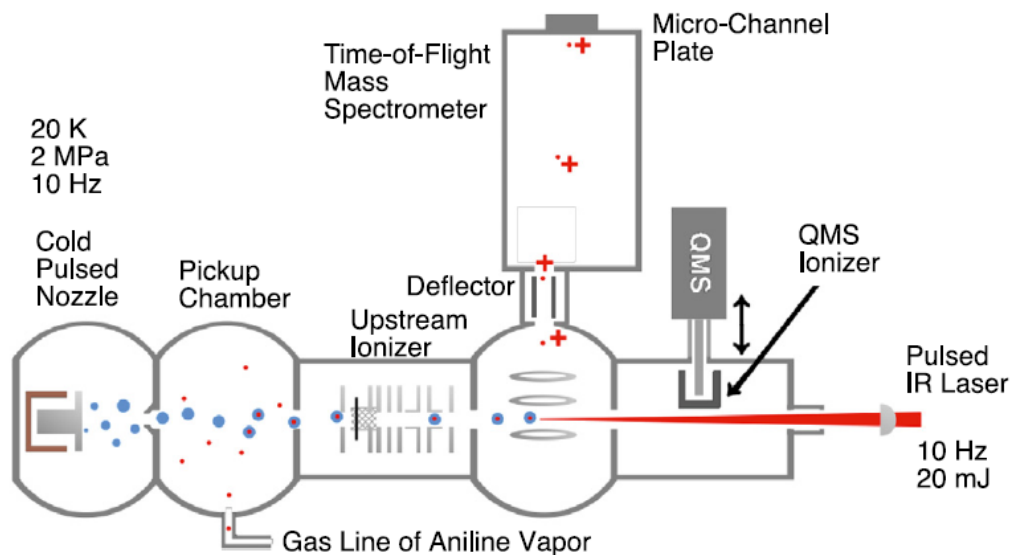


Fig. 1. Experimental setup of this study

Fig. 1 illustrates the experimental setup used in this study. Superfluid helium droplets were produced upon pulsed expansion of a high-pressure (2 MPa) and cold (20 K) helium gas via a cryogenic solenoid valve (General Valve, Series 99).¹⁵ Pulse duration was set to 250 μs on the pulse driver (Parker Hannifin, IOTA-ONE), corresponding to an estimated actual opening time of ~ 70 μs . The droplet beam passed through a 5-mm diameter skimmer and entered a 450-mm long pickup chamber occupied by aniline molecules typically at a few 10^{-4} Pa pressure. Most of the droplets are doped with a single aniline molecule. The aniline-doped helium droplets were ionized via electron ionization in a homemade ionizer system (upstream ionizer) supplying an emission current of 8.5 mA with an electron energy of 100 eV. The upstream ionizer had several electrodes including an Einzel lens system, to eliminate lighter-mass fragments from the beam path.^{3,16-20}

The molecular cations in helium droplets were exposed to counterpropagating nanosecond mid-IR laser pulses in the acceleration region of a time-of-flight (TOF) spectrometer. The 3- μm wavelength pulses, provided from an OPO/OPA laser (LaserVision) pumped by an unseeded Nd:YAG laser, were focused at the center of the acceleration electrodes. A part of the near-infrared light generated in the OPO process was monitored by a wavemeter (HighFinesse, WS-6) to calibrate the laser wavenumber. The maximum pulse energy was 20 mJ, and the nominal laser linewidth was 1 cm^{-1} . The bare ions released by absorbing IR photons repeatedly were accelerated by pulsed voltages applied to the TOF electrodes and detected by a microchannel plate electron multiplier. Synchronization of the whole setup was achieved by delay generators with a repetition rate of 10 Hz. We used a quadrupole mass spectrometer (QMS) (Stanford Research Systems, RGA300) to monitor the droplet beam in separate measurements. The ionizer equipped with QMS (named the QMS ionizer hereafter) was operated at 90 eV electron energy.

We performed the computational calculation to evaluate the experimentally observed vibrational bands. The unrestricted B3LYP density functional method was used with the 6-311+G(3df, 3pd) basis set for the $m/q = 93$ radical cations and the spin-triplet cations at $m/q = 92$ using Gaussian 16.²¹ The restricted version with the same basis set was employed for the closed-shell $m/q = 92$ cations. The potential energy surface calculation for the dissociation of the aniline cation was previously performed by Choe et al.²² and is referred to in the discussions of the present study.

Results

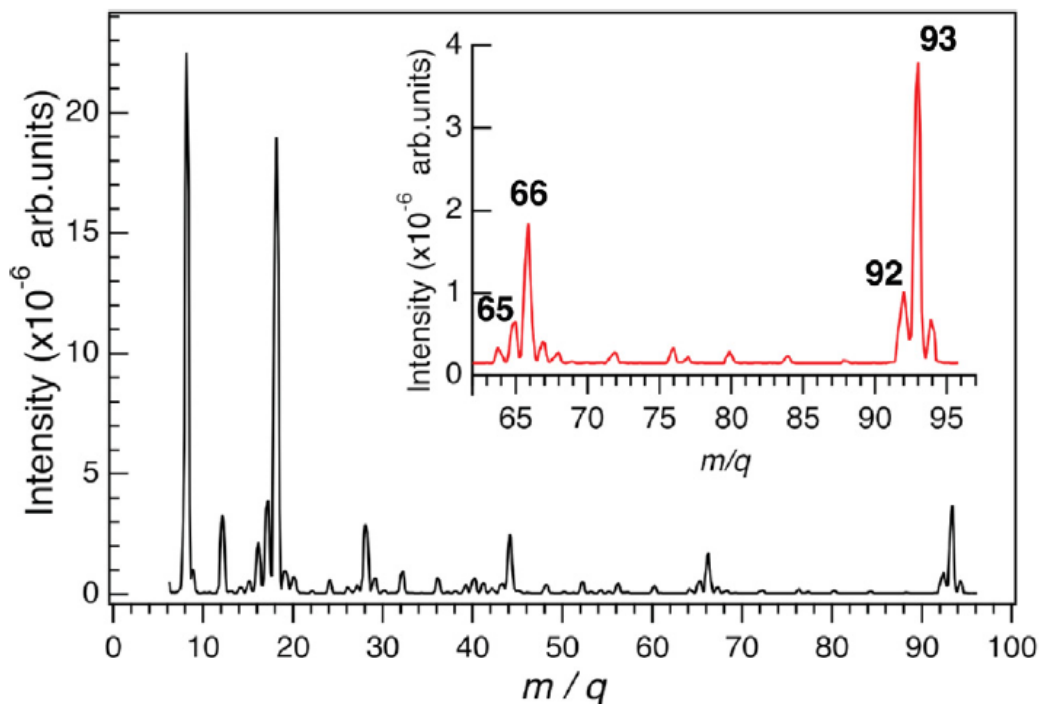


Fig. 2. Mass spectrum of the aniline-captured droplet beam obtained by QMS with its EI ionizer (the QMS ionizer). (Inset) Magnified spectrum above $m/q = 62$.

Fig. 2 shows a mass spectrum measured by QMS when the aniline pressure was 6×10^{-5} Pa. Along with He_n^+ peaks at $m/q = 4n$ (n is an integer) and those originating from the residual gas in the background at $m/q = 18, 28$, and 44 , several peaks attributed to the ionization of aniline in the droplets were observed. We observed the dominant peak due to the aniline cation at $m/q = 93$ and the accompanying weak peak from ^{13}C species at $m/q = 94$. The peak at $m/q = 92$ corresponds to the H-loss aniline cation. The major fragments at $m/q = 66$ and 65 were assigned to the cyclopentadiene radical cation ($\text{c-C}_5\text{H}_6^+$) and cyclopentadienylum ($\text{c-C}_5\text{H}_5^+$, as CPD^+), respectively. In the gas phase study by electron ionization, it is well known that these fragment

five-membered ring species are produced from aniline and other monosubstituted benzenes like phenol.¹¹ It is clear from Fig. 2 that the H_2O^+ peak at $m/q = 18$ was as intense as the helium dimer cation. We estimated the possibility of the H_2O pickup by helium droplets from the residual pressures in the chambers and the droplet size determined below. The average number of H_2O molecules caught by a droplet was found to be 0.07, which is negligible in the next IR measurements. The intense H_2O^+ signal is plausibly explained by the contamination in the QMS setup. The droplet size N_{He} was estimated to be $N_{\text{He}} = 9 \times 10^3$ from the pressure dependence of the $m/q = 93$ signal in Fig. 2 (See the supplemental material). We fixed the aniline pressure at 1.3×10^{-4} Pa in the following measurements.

The observed ion signals in the above measurements were due to the parent and fragment cations ejected from the droplets upon ionization. Hereafter, we focused on the cations isolated in the droplets. We used the upstream ionizer, and the cation-containing droplets were transferred to the laser interaction region for vibrational spectroscopy. Fig. 3 shows the vibrational spectra measured by detecting the ion signals at (a) $m/q = 93$ and (b) 92 in the TOF spectrometer. At $m/q = 93$, we observed two vibrational bands at 3395 and 3490 cm^{-1} , the former of which had been observed in helium droplets by Smolarek et al. and assigned to the N–H symmetric stretching vibration of the aniline cation.⁵ The band at 3490 cm^{-1} was assigned to the N–H anti-symmetric stretching mode of the aniline cation.

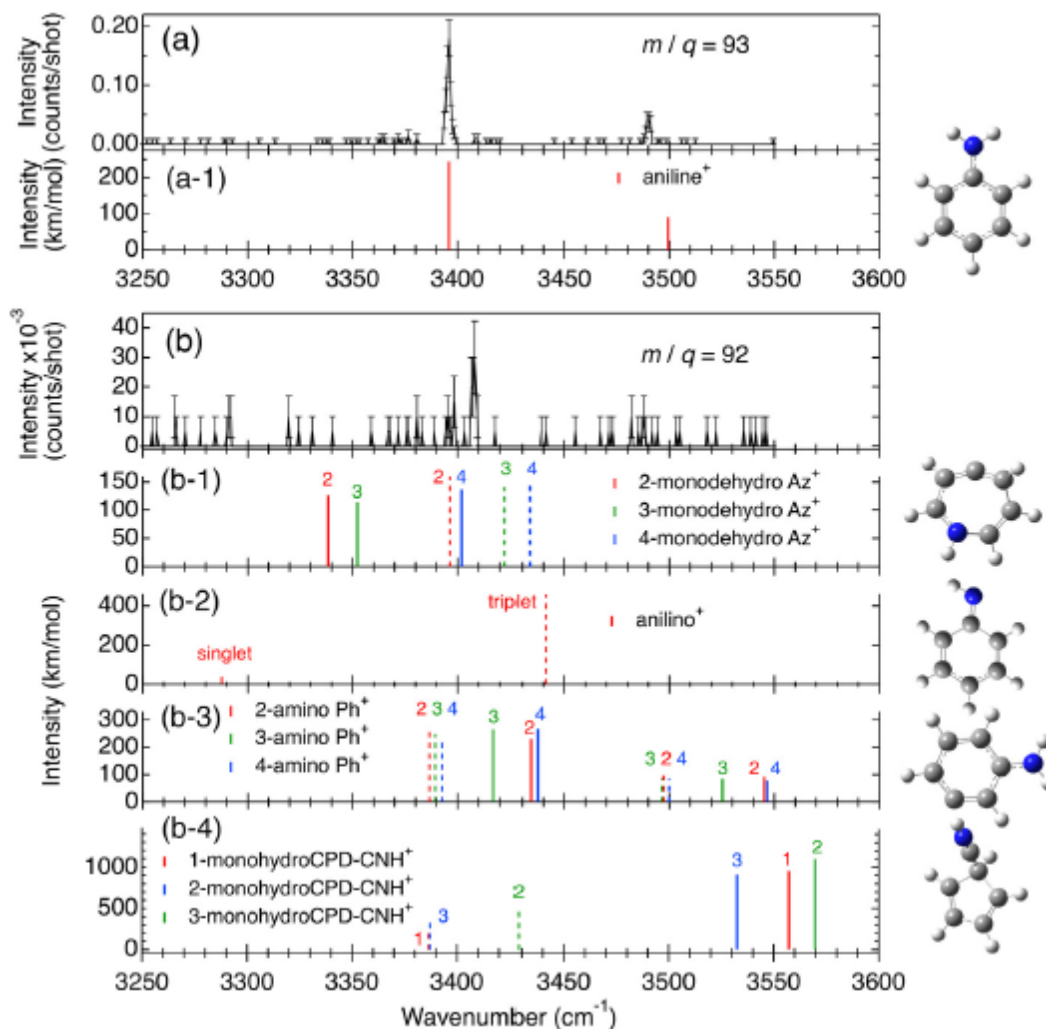


Fig. 3. IR spectra of (a) the aniline cation ($\text{C}_6\text{H}_5\text{-NH}_2^+$, $m/q = 93$) and (b) the H-loss cation at $m/q = 92$. The lower panels show the calculated results for the candidate cations in the singlet (solid lines) and triplet (dashed lines) states. On the right side, the calculated structures as examples are illustrated for the aniline cation (a-1), 4-monodehydro azepinylium (Az) (b-1), anilino cation (b-2), 3-amino phenylium (Ph) (b-3), and 1-monohydro CPD-CNH⁺ (b-4).

For the aniline cation observed in helium droplets, we compared the N-H stretching vibrational bands with those observed in the gas phase⁹ and the Ar-¹⁰ and Ne-tagging¹¹ experiments in Table 1. The amounts of the shifts for both tagging species (aniline⁺-Ar and

aniline⁺–Ne) are a few cm^{−1} from the gas phase values, where the tagging atoms are predicted to locate above the benzene ring and weakly perturb the vibrational motions in the –NH₂ group. Similar shifts were observed in helium droplets, although the helium environment fully surrounds the cation. These small matrix shifts are attributed to the weak intermolecular interaction between the cation and the He atoms. It should be noted that the vibrational bands' linewidths were narrower in helium droplets, partially due to the lower temperature and the smaller inhomogeneity achieved in the droplets.

Table 1

Comparison of the N–H stretching vibrational wavenumbers (cm^{−1}) of the aniline cation.

	Symmetric	Anti-symmetric
He droplets	3395 ^{a,b}	3490 ^a
Gas phase [9]	3393	3486
Ar-tagging [10]	3395	3489
Ne-tagging [11]	3390	3484

The H-loss cation observed at $m/q = 92$ in Fig. 3(b) showed an N–H stretching band at 3406 cm^{−1} and other possible signals whose intensities were comparable to the noise level. Here, we analyzed candidate molecular structures obtained from quantum chemical calculations by comparing their vibrational frequencies with the observed spectrum. First, we performed a calculation on the aniline radical cation as a theoretical reference, ignoring the shift caused in the droplet. The panel (a-1) of Fig. 3 shows the result of the calculations. The scaling factor of 0.960

was adopted for the best reproducibility of the experimental band frequency for the N–H symmetric stretch of the aniline cations in He droplets.

Table 2: Comparison of N–H vibrational frequency calculations for the $m/q = 92$ cations in the singlet/triplet states.

Cation species (Calculation)	Wavenumbers (cm ⁻¹) Singlet/triplet	Energy ^c (eV) Singlet/triplet
1-monohydro CPD–CNH	3557/3387	11.3/14.1
2-monohydro CPD–CNH	3533/3429	11.6/13.4
3-monohydro CPD–CNH	3570/3387	12.0/13.4
anilino (C ₆ H ₅ =NH)	3288/3441	11.9/12.8
2-amino Ph	3434 ^a /3387 ^a , 3545 ^b /3497 ^b	12.9/12.5
3-amino Ph	3417 ^a /3389 ^a , 3525 ^b /3497 ^b	12.5/12.9
4-amino Ph	3437 ^a /3393 ^a , 3546 ^b /3500 ^b	12.8/12.4
2-monodehydro Az	3338/3396	12.5/13.2
3-monodehydro Az	3352/3422	12.5/13.2
4-monodehydro Az	3402/3434	12.5/13.1
Experiment	3406	-

^a Symmetric.

^b Anti-symmetric.

^c Energy relative to neutral aniline. ZPV (zero-point vibration) corrections are included.

Fig. 3(b) and Table 2 summarize the comparison among the experimental value and the computational results for possible candidates as the isomeric H-loss cations at $m/q = 92$. The H radical loss from the $m/q = 93$ radical cation results in the ionic fragment being either in a singlet or triplet state, and therefore the N–H stretching frequencies of both cases are depicted in Fig. 3 panels (b-1) to (b-4). We adopted the same scaling factor of 0.960 as the aniline cation. The corresponding electronic energies are also included in Table 2.

Azepinyliums (Az) (ϵ -C₆NH₆⁺, $m/q = 92$) have the H-loss structures from the cationic form of a seven-membered ring called azepine (ϵ -C₆NH₇, $m/q = 93$), and their most stable structure is the H-loss type from the N–H bond. However, this structure is clearly not responsible for the observed band in the N–H stretching region. In Fig. 3(b-1) we calculated the structures and vibrational frequencies of other H-loss azepinyliums, i.e., 2-, 3-, and 4-monodehydro Az cations produced by H-atom dissociation from the corresponding C atoms. Their singlet N–H vibrational bands were found to be located at 3338, 3352, and 3402 cm⁻¹, respectively. The vibrational band of N–H stretch for 4- monodehydro Az matches well with the experimental spectrum at $m/q = 92$. This suggests that the 4-monodehydro Az cation is a good candidate for the observed band. All triplet bands might also be the possible candidates, though their energies are predicted to be higher than the singlet species.

The anilino cation (ϵ -[C₆H₅=NH]⁺) has a –NH substituent, that is, the H-loss structure from the amino group (–NH₂) of the aniline cation. Its N–H mode in the singlet state was calculated to appear at 3288 cm⁻¹ (see Fig. 3(b-2)), which is far red-shifted (–107 cm⁻¹) from the aniline cation due to the neighbor C=N double bond. The existence of this species might be supported by the

spiky signals in the corresponding region in the observed spectrum, or by the proximity of the predicted band at 3441 cm^{-1} as for the higher-energy triplet.

As shown in Fig. 3(b-3), additional calculations were performed for amino phenylium ($\sigma\text{-C}_6\text{H}_4\text{-NH}_2^+$) containing the amino group (-NH_2). The computed spectra of these amino phenylium (Ph) cations also show the symmetric N–H stretching mode close to the band observed in the experimental spectrum. Interestingly, the triplet species of the 2- and 4- amino Ph cations have lower energy than the singlet species. It is due to the delocalization effect in the π -electron system in these triplet cations, as evidenced in the case of the naphthyl cation.²³ Their anti-symmetric bands, whose intensities are about 1/3 of the symmetric bands, appear to overlap with the noise level in the observed spectrum.

We also performed DFT calculations for the five-membered ring monohydro CPD– CNH^+ ($\sigma\text{-C}_5\text{H}_5\text{-CNH}^+$) cations, whose production has been reported by Rap et al. in the gas phase upon electron ionization of neutral aniline molecules based on the vibrational spectra in the range of $550\text{--}1800\text{ cm}^{-1}$.¹² They discussed their relevance to the neutral 2- and 3-monohydrocyano CPD ($\sigma\text{-C}_5\text{H}_5\text{-CN}$) molecules recently found in interstellar space^{13,14} and the possibility of their existence in Titan's atmosphere.¹² Our theoretical calculations show that the singlet 1-, 2-, and 3-monohydro CPD– CNH^+ cations have the blue-shifted N–H stretching mode at 3557 , 3533 , and 3570 cm^{-1} , respectively. The existence of these bands is not clear in our spectrum due to the limited signal-to-noise ratio and the limited measured spectral range. The corresponding triplet species show the N–H bands in the vicinity of the observed band, exhibiting the possibility among the candidate isomers.

Discussion

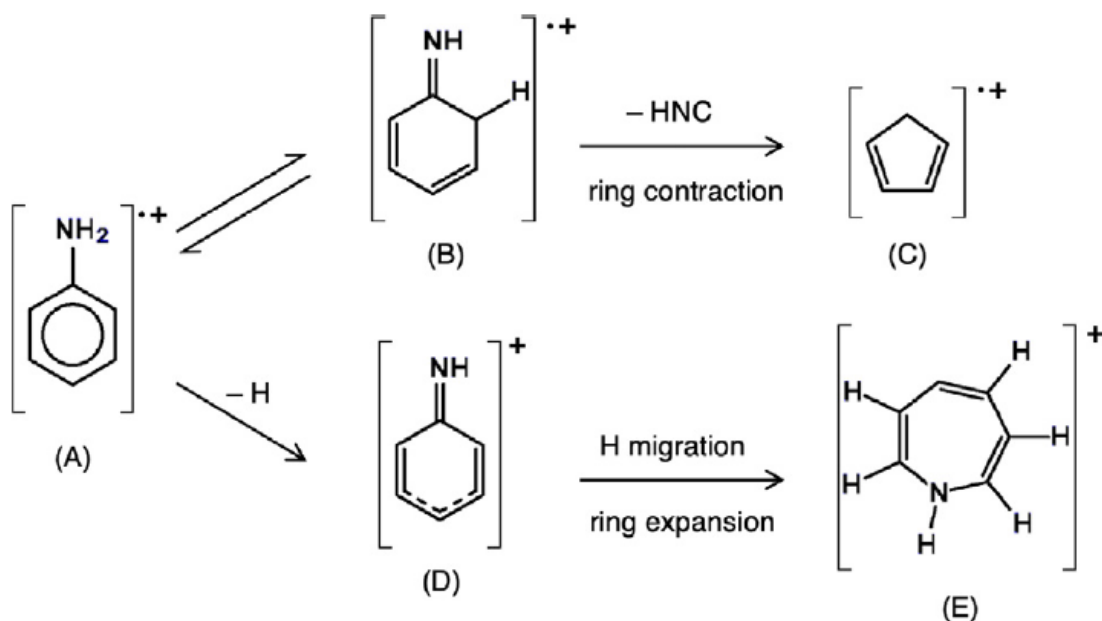


Fig. 4. Reaction pathways from aniline cations (A) considered in this study. Via tautomerization to the [cyclohexa-2,4-dien-1-imine] $^+$ (B), the cyclopentadiene radical cation (C) is produced by the ring contraction. In the case of the H-loss process, a new ring expansion reaction path through anilino $^+$ (D) is proposed with the product of the seven-membered ring 4-monodehydro azepinylium (E).

Molecular cations are likely produced via charge transfer in helium droplets after electron ionization of the droplets containing neutral parent species. It is known that the He_2^+ dimer rapidly forms after the direct ionization of a He atom on the droplet surface. The binding energy of He_2^+ is about 2 eV.²⁴ Although the detailed process that makes the stable isolation of the molecular ion possible in the droplet is yet to be elucidated, we expect that a large amount of excess energy is generated due to the difference in the ionization potentials between He (or He_2) and the target molecule. In the present case, aniline has an ionization potential of 7.7 eV.²⁵ The charge transfer process between aniline and He^+ (or He_2^+) will generate an excess energy of at least 15 eV.

Our previous study ⁴ produced a meta-stable structure of the water dimer cation. Removal of the excess energy, ~ 12 eV in this case, by He evaporation was so efficient that the hemibonded dimer cation, which is unstable by <1 eV to the most stable form of the proton-transferred cation, coexists in the droplet beam, even though the potential barrier is as low as <0.3 eV. Such an efficient kinetic trapping effect is also expected for the unimolecular ionization reaction of aniline, possibly leading to the observation of the reaction intermediates.

In the highly excited aniline cation (A) (Fig. 4) produced by electron ionization, the $-\text{NH}_2^+$ substituent attacks the 1C–2C π bond to make another H-bond at the 2C atom leading to the intermediate iminetautomer, [cyclohexa-2,4-dien-1-imine]⁺ ($\text{c-C}_6\text{H}_6=\text{NH}^+$) at $m/q = 93$ (B). This intermediate has been confirmed to exist by theoretical calculations ^{11,22} but was not detected in the cryogenic ion trap experiment. ¹¹ The $\text{c-C}_5\text{H}_6^+$ fragment (C) is produced by the ring contraction via this imine intermediate as the rate-determining step. In the current study and the work by Smolarek et al. ⁵ only the N–H bands attributed to the aniline cation were found at the mass of $m/q = 93$ in helium droplets. Choe et al. ²² performed the kinetic analysis based on the RRKM treatment in the gas phase and found that the production rate of $\text{c-C}_5\text{H}_6^+$ increases with the internal energy, reaching 109 s^{-1} at the excess energy around 8 eV measured from the aniline cation. Assuming the excess energy of 15 eV as discussed above and the same RRKM treatment in helium droplets, this rate becomes plausibly faster than 1011 s^{-1} . The non-existence of the imine cation (B) in He droplets may suggest that the effective cooling rate in the droplets is slower than this estimation, although further studies will be required to understand the cooling process after the ionization.

As for the $m/q=92$ cation, Rap et al.¹² found the H-loss product 2- and 3-monohydro CPD–CNH⁺ cations in their cold ion trap experiment using electron ionization at 15 eV. They concluded that the N-bearing aromatic compounds likely isomerize to the five-membered ring structure produced via the successive fragmentation processes by the HNC loss (to ϵ -C₅H₆⁺) and the H-loss (to monohydro CPD–CNH⁺). These processes are still to occur in He droplets, as evidenced by the observation of ϵ -C₅H₆⁺ in Fig. 2 and the possibility of monohydro CPD–CNH⁺ cations in Fig. 3. However, the production of other candidates requires different pathways. In particular, the production of the 4-monodehydro azepinylium (Az) cation requires the ring expansion reaction upon ionization. The extrapolation of the above RRKM study by Choe et al.²² predicts that the H-loss reaction toward the anilino cation (ϵ -[C₆H₅=NH]⁺) (D) has a rate comparable to that for the fragmentation path to ϵ -C₅H₆⁺ above the excess energy of 12 eV. Because the excess energy in the present study is as high as 15 eV, we propose the 4-monodehydro azepinylium (E) as the product along this reaction pathway with the subsequent isomerization to the seven membered ring structure. This reaction path should also include the H-hole migration to the 4C position. It is noted that the ring expansion reaction producing the seven-membered ring ions is common to other mono-substituted benzenes like phenol²⁶ and toluene.²⁷

Conclusions

Electron ionization of aniline ($\text{c-C}_6\text{H}_5\text{-NH}_2$) in helium droplets studied here illustrated how the kinetic trapping effect in the cold helium environment contributes during the unimolecular ionization of the aromatic molecule. The cationic imine tautomer, which is proposed as an intermediate in the reaction pathway leading to the cyclopentadiene radical cation ($\text{c-C}_5\text{H}_6^+$) at $m/q = 66$, was not observed despite the expected large kinetic trapping effect of helium droplets. Instead, we identified only the aniline cation ($\text{c-C}_6\text{H}_5\text{-NH}_2^+$) at this m/q , and the observed N–H stretching bands show small matrix shifts in helium droplets.

The H-loss cation from the same parent ion showed an N–H band in its vibrational spectrum, whose assignment was performed with the aid of DFT calculations. We found as one of the candidate structures the seven-membered ring 4-monodehydro azepinylium ($\text{c-C}_6\text{NH}_6^+$). The large excess energy of ~ 15 eV in the ionization may open a new reaction pathway that favors H-loss and ring expansion. Extensive quantum chemical calculations are required to confirm the proposed reaction path combined with molecular dynamics simulation along various reaction pathways. The study with other mono-substituted benzenes in helium droplets will contribute to further understanding of the proposed reaction mechanism under rapid cooling in the droplets.

Acknowledgement

We thank Andrey F. Vilesov for his valuable advice and James R. Harries for the critical reading of the manuscript. A.I. acknowledges the support by JST, the establishment of university fellowships towards the creation of science technology innovation, Japan, Grant JPMJFS2139. The authors thank the financial support from JSPS (Japan) KAKENHI Grants JP20H04464, 21H04644 and 23H03670 (S.K.), RIKEN Incentive Research Projects (S.K.), Japan, and RIKEN Pioneering Projects, Japan. Research visit of A. Singh to RIKEN was supported by the National Science Foundation, United States under Grant CHE-2102318 and an international collaboration fund from RIKEN, Japan.

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