Photodissociation dynamics of pyridine

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Photodissociation of pyridine, 2,6-d2-pyridine, and d5-pyridine at 193 and 248 nm was investigated separately using multimass ion imaging techniques. Six dissociation channels were observed at 193 nm, including C5NH5 → C4H4 + HCN (10%) and five ring opening dissociation channels, C5NH5 → C6H6 + HCN, C6NH3 → C5H5 + C2NH2, C2NH2 → C2H4 + C3NH, C5NH5 → C5H5 + CH3 (14%), and C5NH5 → C2H2 + C4NH3. Extensive H and D atom exchanges of 2,6-d2-pyridine prior to dissociation were observed. Photofragment translational energy distributions and dissociation rates indicate that dissociation occurs in the ground electronic state after internal conversion. The dissociation rate of pyridine excited by 248-nm photons was too slow to be measured, and the upper limit of the dissociation rate was estimated to be 2 × 10^3 s^-1. Comparisons with potential energies obtained from ab initio calculations and dissociation rates obtained from the Rice-Ramsperger-Kassel-Marcus theory have been made. © 2005 American Institute of Physics.

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I. INTRODUCTION

The thermal decomposition processes of aromatic molecules, such as benzene and pyridine, have been studied extensively. Early shock-tube studies and high-temperature flow tube investigations showed that hydrogen, methane, ethylene, acetylene, and biphenyl are the major products from thermal decomposition of benzene. The thermal decomposition of pyridine also has been studied at various temperatures. The major products include hydrogen cyanide, methane, acetylene, cyanacetylene, acrylonitrile, benzonitrile, quinoline, acetonitrile, benzene, and naphthalene. A commonly accepted mechanism for the pyrolysis of these two molecules involves a series of complicated reactions initiated by the H atom loss reaction.

The main photoproducts of benzene vapor at 184.9 nm were reported to be an isomer of benzenene, subsequently identified as fulvene, and polymers. Cis- and trans-1,3-hexadien-5-yn-1 and ethene, acetylene, hydrogen, and acetylene were also observed. Similar to benzene, photolysis of pyridine in the UV region produced H2, C2H2, HCN, C2H4, and brown deposit. The photoproducts of methane, ethane, ethylene, acetylene, and HCN indicate the existence of ring opening photodissociation processes for both benzene and pyridine.

During the past few decades, the advancement of the application of lasers in combination with the molecular-beam technique has made a great impact on the understanding of primary photodissociation processes. The capability to detect the nascent photodissociation products has provided extremely detailed information on the photodissociation mechanisms. Photodissociation of benzene at 193 nm has been investigated in a molecular beam. In addition to the H atom elimination, H2 elimination and a ring opening dissociation channel C6H6 → C5H5 + CH3 were reported. In order to produce the fragments C2H2 and CH3, H atoms in benzene must migrate until one carbon atom gathers three H atoms and then C–C bond breaks. This must involve successive H atom migration isomerizations. The dissociation mechanism must be very complicated. This ring opening dissociation channel provides a possible explanation of the photoproducts such as methane and ethane from benzene. Since benzene and pyridine have the analogous structure and share similar photochemical properties, the parallel ring opening dissociation channels are expected to occur in pyridine. Indeed, photodissociation of pyridine in a molecular beam has been investigated at 193 nm. H atom elimination as well as ring opening dissociation channels has been reported.

However, the aromatic ring is a very stable structure. A relatively large energy is required to open the ring and dissociate the ring into two fragments. Recent ab initio calculations showed that the dissociation barrier of benzene ring opening dissociation channel is very close to the 193-nm photon energy. The branching ratio of the ring opening channel at 193 nm is thus expected to be negligible. Consequently, the dissociation mechanism of the ring opening channel remained unclear. Recently, we have constructed a new apparatus to study the photodissociation of aromatic molecules. The apparatus has a very high sensitivity to detect photofragments. The intensity of the photolysis laser beam employed in the study can be much lower than that in the previous studies. In our study of benzene, the 193-nm photolysis laser beam intensity was in the range of...
0.1–10 mJ/cm² which is about 100 times smaller than the laser intensity used in the previous study. With such intensity, the probability of one-photon absorption saturation is very small. The photolysis photon number dependence in each dissociation channel therefore can be accurately measured. It was found that H atom elimination is the only one-photon dissociation channel, and the corresponding dissociation rate is $1 \pm 0.2 \times 10^5$ s⁻¹. Although the ring opening dissociation channel, $\text{C}_6\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$, was confirmed by the photofragment momentum match, it resulted from two-photon dissociation. Indeed, additional ring opening dissociation channels were also observed from one-photon dissociation at 157 nm.  

In this work, we report a study of pyridine photodissociation using these new techniques. Photofragment translational energy distributions and dissociation rates of pyridine, $2,6$-$d_2$-pyridine, and $d_5$-pyridine at 193 and 248 nm are measured. New dissociation channels are detected. The results are compared to ab initio calculations. New isomerization and dissociation mechanisms are proposed.

II. EXPERIMENT

The experimental techniques have been described in detail in our previous reports, and only a brief account is given here. Pyridine vapor was formed by flowing ultrapure He (or Ne) at pressures of 400 Torr through a reservoir filled with pyridine sample at 10 °C. The pyridine/He (or Ne) mixture was then expanded through a 500-μm high-temperature (70 °C) pulsed nozzle to form the molecular beam. Molecules in the molecular beam were photodissociated by UV laser pulses, and fragments were then ionized by vacuum UV (VUV) laser pulses. The distance and time delay between the VUV laser pulse and the photolysis laser pulse were set such that the VUV laser beam passed through the center of mass of the dissociation products, and generated a line segment of photofragment ions through the center of mass of the dissociation products by photionization. To separate the different masses within the ion segment, a pulsed electric field was used to extract the ions into a mass spectrometer after ionization. At the exit port of the mass spectrometer, a two-dimensional ion detector was used to detect the ion positions and intensity distribution. In this two-dimensional detector, one direction was the recoil velocity axis and the other was the mass axis.

Depending on the velocity of the molecular beam, it was necessary to change the distance between the photolysis laser beam and the VUV laser beam to match the delay time between these two laser pulses to ensure that the ionization laser would pass through the center of mass of the products. The change of the distance between the two laser beams changed the length of the fragment ion segment in the image. If the molecules were not dissociated after the absorption of UV photons, these high internal energy molecules would remain within the molecular beam. They flew with the same velocity (molecular-beam velocity) to the ionization region and were ionized by the VUV laser. The wavelengths of the VUV lasers used in this experiment were 118.2 and 88.6 nm. For the wavelength of 118.2 nm, the photon energy was only large enough to ionize parent molecules. The dissociation of parent molecule cations would not occur with the energy left after the ionization by the 118.2-nm laser beam. However, the dissociation occurred following the 118.2-nm photoionization for those hot molecules, which absorbed UV photon and did not dissociate into fragments before the arrival of the 118.2-nm laser beam. The ion image of the dissociative ionization was different from the image due to the dissociation products of neutral parent molecules. Since ionization and dissociation occurred at the same position, the image of dissociative ionization was a two-dimensional (2D) projection of photofragment ion’s three-dimensional (3D) recoil velocity distribution. It was a disklike image, rather than a line-shape image. In addition, the size of image from the dissociative ionization would not change with the delay time. On the other hand, if fragments cracked into small ionic species upon the VUV photoionization, the shape of the image was also disklike, but the width of the image changed with the delay time. From the shape of the image and its change with the delay time, the images from dissociation of neutral molecules, dissociative ionization of undissociated excited molecules, and the fragment cracking can be easily distinguished.

The dissociation rate was obtained from the measurements of product growth and disklike image intensity decay with respect to the delay time between the pump- and probe-laser pulses.

III. RESULTS

A. Pyridine

Fragments of $m/e=78$, 65, 64, 52, 51, 40, 39, 28, and 15 were observed from the photodissociation of $h_5$-pyridine at 193 nm using the 118.2-nm VUV laser beam. Photolysis laser intensities in the region of 0.131–7.84 mJ/cm² were used to determine the photon number dependence of these fragments. Since the absorption cross section of pyridine at 193 nm is $1.5 \times 10^{-17}$ cm², the photolysis laser intensity we used in this experiment does not saturate this transition. After the absorption of one 193-nm photon, the absorption cross section for the second 193-nm photon absorption may change. However, except the second photon absorption cross section increases by a factor of 1000 and becomes abnormally as large as $10^{-14}$ cm², the second photon absorption will not be saturated at such a low photolysis laser intensity. As a result, dependence of photofragment ion intensities on the number of photolysis photons can be determined. It shows that all photofragments resulted from one-photon dissociation.

Figure 1 depicts the photofragment ion images obtained from the photodissociation of pyridine at 193 nm using the 118.2-nm VUV laser beam. Fragment $m/e=65$ has the same intensity profile as that of fragment $m/e=64$. The intensity of $m/e=65$ is about 6% of $m/e=64$, indicating that it is a $^{13}$C isotopomer of $m/e=64$. Fragments $m/e=15$, 39, 40, and 64 have line-shape images. They resulted from the dissociation of pyridine. The images of fragments $m/e=28$, 52, and 78...
have two components: a line-shape component located on both wings and a disklike component located at the center. As the delay time between the pump- and the probe-laser pulses increased, the component on both wings moved rapidly toward the outside. On the other hand, the size of the disklike image at the center did not change, but the intensity decreased with the increase of the delay time. The line-shape component resulted from the fragments of pyridine with large recoil velocity and the disklike component was from the dissociative ionization of undissociated excited pyridine. The image of \( m/e = 51 \) is pure disklike, however, the size of the disk slowly changes with the delay time. Instead of dissociative ionization from the undissociated parent molecules, it must be from the dissociative ionization of some heavy fragments. From the width of the disklike image of \( m/e = 51 \), it can be determined that it is from the dissociative ionization of the fragment \( \text{C}_5\text{NH}_4^+ \).

Figure 2 illustrates the photofragment ion images in the region \( m/e = 26–28 \) and 50–53 using 88.6-nm photoionization laser beam. Additional fragments, such as \( m/e = 53, 27, \) and 26 which have higher ionization potentials and cannot be ionized by 118.2-nm photons, were observed using this short-wavelength VUV laser beam.

The possible reactions are described as follows:

\[
\text{C}_3\text{NH}_3 + h\nu(193 \text{ nm}) \rightarrow \text{C}_3\text{NH}_4^+, \quad (1)
\]

\[
\text{C}_3\text{NH}_3^+ \rightarrow \text{C}_3\text{NH}_4 + \text{H}, \quad \text{(2)}
\]

\[
\text{C}_3\text{NH}_3^+ \rightarrow \text{C}_4\text{H}_4 + \text{HCN}, \quad \text{(3a)}
\]

\[
\text{C}_3\text{NH}_3^+ \rightarrow \text{C}_3\text{NH}_2 + \text{C}_2\text{H}_3, \quad \text{(3b)}
\]

\[
\text{C}_3\text{NH}_3^+ \rightarrow \text{C}_4\text{H}_2 + \text{CH}_3, \quad \text{(3c)}
\]

\[
\text{C}_3\text{NH}_3^+ \rightarrow \text{C}_5\text{H}_4 + \text{NH}, \quad \text{(4b)}
\]

\[
\text{C}_3\text{NH}_3^+ \rightarrow \text{CN} + \text{C}_4\text{H}_5. \quad \text{(7b)}
\]

\( \text{C}_3\text{NH}_3^+ \) represents the pyridine molecule after absorption of one 193-nm photon. The molecule can be in the initial electronic excited state, or in the lower electronic state after internal conversion or intersystem crossing. We will show in the Discussion section that \( \text{C}_3\text{NH}_4^+ \) represents the highly vibrationally excited pyridine in the ground electronic state after internal conversion. The VUV photon energy of 118.2 nm is 10.5 eV, which is lower than the ionization energies of HCN and NH, but it is higher than the ionization energies of \( \text{C}_2\text{H}_3 \) and \( \text{CH}_3 \). The observation of ions \( m/e = 15 \) and no observation of ions \( m/e = 27 \) when the 118.2-nm laser beam was used suggest the occurrence of reactions (3a) and (4a), instead of (3b) and (4b). Fragment \( m/e = 53 \) was only observed when the VUV laser beam was 88.6 nm. It indicates that \( \text{C}_3\text{NH}_3 \) in reaction (7a) is 2-propenenitrile (ionization potential 10.91 eV) and reaction (7b) does not occur. Reactions (5a) and (6a) cannot be distinguished from (5b) and (6b) due to the same \( m/e \) values of fragments. However, they can be determined using isotope-substituted \( d_5 \)-pyridine, as illustrated in Sec. III B. The dissociation channels are reactions (5a) and (6a). In fact, reactions (3a), (4a), and (7a) can also be confirmed using isotope-substituted \( d_5 \)-pyridine.

The products from these reactions were ionized by 118.2-nm photoionization laser pulses and produced line-shape images.

\[
\text{C}_3\text{NH}_4 + h\nu(118 \text{ nm}) \rightarrow \text{C}_3\text{NH}_4^+ + e^- , \quad \text{(8)}
\]

\[
\text{C}_4\text{H}_4 + h\nu(118 \text{ nm}) \rightarrow \text{C}_4\text{H}_4^+ + e^- , \quad \text{(9)}
\]

\[
\text{C}_4\text{NH}_2 + h\nu(118 \text{ nm}) \rightarrow \text{C}_4\text{NH}_2^+ + e^- , \quad \text{(10)}
\]

\[
\text{CH}_3 + h\nu(118 \text{ nm}) \rightarrow \text{CH}_3^+ + e^- , \quad \text{(11)}
\]

\[
\text{C}_5\text{H}_4 + h\nu(118 \text{ nm}) \rightarrow \text{C}_5\text{H}_4^+ + e^- , \quad \text{(12)}
\]
The disklike image resulted from the dissociative ionization of undissociated excited pyridine due to the slow dissociation rate at 193 nm, or from the fragment cracking during the ionization.

\[
\text{C}_2\text{NH}_3 + h\nu(118 \text{ nm}) \rightarrow \text{C}_2\text{NH}_2^+ + \text{e}^-.
\]

\[
\text{C}_3\text{H}_3 + h\nu(118 \text{ nm}) \rightarrow \text{C}_3\text{H}_2^+ + \text{e}^-.
\]

The disklike images located at the center of images \( m/e = 26 \) and 27 also have the contributions from the reactions of fragment cracking due to the large photon energy at 88.6 nm.

\[
\text{C}_3\text{NH}_3 + h\nu(88.6 \text{ nm}) \rightarrow \text{C}_2\text{H}_2^+ + \text{HCN} + \text{e}^-.
\]

\[
\text{C}_4\text{H}_4 + h\nu(88.6 \text{ nm}) \rightarrow \text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_2 + \text{e}^-.
\]

\[
\text{C}_2\text{H}_4 + h\nu(88.6 \text{ nm}) \rightarrow \text{C}_2\text{H}_2^+ + \text{H}_2 + \text{e}^-.
\]

\[
\text{C}_4\text{H}_4 + h\nu(88.6 \text{ nm}) \rightarrow \text{C}_2\text{H}_3^+ + \text{H} + \text{e}^-.
\]

The analysis of momentum matches between the heavy and light fragment partners was performed to further confirm the dissociation channels, as shown in Fig. 3. The momentum matches also exclude the contribution from three-body dissociation, such as the dissociation of clusters or the contribution from cation dissociation.

The photofragment translational energy distributions obtained from the images are shown in Fig. 4. For reactions (3a), (5a), and (7a), the average released translational energies are large, and the peaks of the distribution are located at 27, 20, and 25 kcal/mol, respectively. The maximum translational energies reach the maximum available energies of these reactions. On the other hand, the average released translational energies for reactions (2), (4a), and (6a) are all very small. The peaks of the distribution are located very close to zero and the probabilities decrease monotonically with increasing the translational energy.

The dissociation rate of the neutral excited pyridine molecules due to the 193-nm photon excitation was measured from the intensity changes of these disklike images as well as from the product growths with respect to the delay time between pump- and probe-laser pulses. They are shown in Fig. 5. A dissociation rate of \( 7.7 \times 10^9 \text{ s}^{-1} \) was obtained from the fit of the experimental data to \( A \times \exp(-k_1t) + B \times (1 - \exp(-k_2t)) \). The first term represents the contribution from dissociative ionization, and the second term represents the product generated from neutral molecule dissociation. At long delay time, some products \((m/e=52)\) with large recoil velocity flew away from the detection region and the corresponding ion intensities are lower than that from the calculation.

The quantum yields of reactions (2) and (4a) can be...
estimated using the following argument. Quantum yield of CH3 from the photodissociation of ethylbenzene at 193-nm C6H5C2H5 \rightarrow C6H5CH2 +CH3 is well known. Therefore, the quantum yield of reaction (4a) C5NH5 \rightarrow C5NH4 +H can be obtained by comparing the CH3-ion intensities from the photodissociation of ethylbenzene and pyridine after the normalization of each concentration in the molecular beam and absorption cross section at 193 nm. A quantum yield of \( \Phi = 0.14 \) was obtained for reaction (4a). The quantum yield of the reaction C5NH5 \rightarrow C5NH4 +H can be estimated by comparing to the fragment intensity of C5NH4 from picoline. In the photodissociation of picoline, one of the major channels is C5NH4CH3 \rightarrow C5NH4 +CH3. The relative ion intensity of C5NH4+ and CH3+ measured by the same VUV wavelength (118.2 nm) is 2.9:1. Since these two fragments are from the same dissociation channel of picoline and the VUV photon energy is much higher than the ionization potential of these two fragments, the relative ion intensity gives a good estimation of the relative ionization cross section of these two fragments, the relative ion intensity gives a good estimation of the relative ionization cross section of these two fragments, the relative ionization cross section of the other fragments, the quantum yields of the other channels cannot be obtained at this moment.

Photodissociation of pyridine at 248 nm was also investigated. Fragment ions of \( m/e = 78, 53, 52, 39, \) and 28 were observed using the 118.2-nm VUV laser beam. However, they all have disklike images, and the sizes of these disklike images do not change with the delay time. Some of them are shown in Figs. 6(a) and 6(b). The intensities of these disklike images did not change with the delay time, as shown in Fig. 6(c). This is because the lifetime is too long to be measured in our instrument. The upper limit of the dissociation rate was estimated to be \( 2 \times 10^3 \) s\(^{-1}\).

B. \( d_5 \)-pyridine

As shown in Fig. 7, images similar to those for h5-pyridine were observed from the photodissociation of \( d_5 \)-pyridine at 193 nm. It is interesting to note that the image of \( m/e = 42 \) was observed. No image corresponding to \( m/e = 40 \) or 44 was observed. Therefore the dissociation must occur through reaction (6a), instead of reaction (6b).

FIG. 5. Intensity changes of these disklike images as well as the product growth with respect to the delay time between pump- and probe-laser pulses. The VUV laser is 118.2 nm. The solid squares are the experimental data. The solid lines are the fit to \( A \times \exp(-k_1 t) + B \times (1 - \exp(-k_1 t)) \).

FIG. 6. (a) Image of \( m/e = 39 \). (b) Image intensity profiles of \( m/e = 39 \) at delay times of 3 \( \mu \)s (thick) and 59 \( \mu \)s (thin). (c) Image intensities as a function of delay time at 1.4 mJ/cm\(^2\) of 248 nm. Open square: \( m/e = 78 \), open circle: \( m/e = 52 \), open triangle: \( m/e = 39 \), and solid diamond: \( m/e = 28 \). The wavelength of the VUV laser is 118.2 nm.

FIG. 7. Photofragment ion images from the photodissociation of \( d_5 \)-pyridine at 193 nm. The wavelength of the VUV laser is 118.2 nm.
similar argument can be applied to show the existence of reaction (5a), instead of reaction (5b). Some of the decays of the disklike images and the growths of the products from the photodissociation of $d_5$-pyridine are shown in Fig. 8. The results indicate that the dissociation rate is $2.5 \times 10^6$ s$^{-1}$, which is slower than that of pyridine by a factor of 3.

C. 2,6-$d_2$-pyridine

Photofragment ion images obtained from the photodissociation of 2,6-$d_2$-pyridine at 193 nm are shown in Fig. 9. Images corresponding to substituted fragments with different numbers of D atoms were all observed. These fragments clearly indicate that the exchange between D and H atoms occurs before dissociation. The respective ratios between various isotope-substituted fragments from the experimental measurement are compared to the statistical values, as given in Table I. This suggests that the isotopic scrambling between D and H atoms in 2,6-$d_2$-pyridine is almost complete before the dissociation occurs.

IV. DISCUSSION

The electronic absorption spectrum of pyridine is dominated by three bands at about 5.0, 6.4, and 7.2 eV, which are associated with the $n$-$\pi^*$ valence excitation to the $S_2$, $S_3$, and $S_4$ states, respectively. The $n$-$\pi^*$ excitation to $S_1$ has a smaller cross section and is located at the shoulder of the $S_2$ absorption band. Very low fluorescence quantum yields of $5.9 \times 10^{-5}$ and $0.27 \times 10^{-5}$ were measured upon the excitation into the $S_1$ and $S_2$ states, respectively. Low fluorescence quantum yield and short lifetime of $S_1$ become as short as a few picoseconds. Photoisomerization of pyridine into Dewar-type valence isomers has been observed in solutions and matrices upon excitation into the $S_2$ state. Femtosecond time-resolved absorption spectroscopy in the condensed phase has been employed to study the excited-state dynamics of pyridine. Nonradiative deactivation of the $S_1$ state occurs in 9–23 ps and it is to a large extent due to intersystem crossing. Photoexcitation to the $S_2$ state leads to the formation of the fulvenic form of pyridine through the conical intersection. Recently, femtosecond time-resolved mass-spectrometric experiments on gas phase pyridine below the channel-three threshold have revealed a fast decay component of 400 fs, which described the initial motion on the potential surface of pyridine, and slower components of 3.5 and 15 ps which were assigned to the formation of the Dewar and Hückel isomers, respectively. Another isomer of ring-opened diradical structure resulting from the excited pyridine was observed above the channel-three threshold using ultrafast electron diffraction.

Absorption of 248- and 193-nm photons corresponds to the excitation of pyridine to $S_2$ and $S_3$, respectively. The dissociation was too slow to be observed at 248 nm. On the other hand, the experimental results at 193 nm show that the wavelength is shorter than 275 nm. This is interpreted as the result from a nonradiative pathway, termed “channel three,” by which vibrational energy in excess of $\sim 1600$ cm$^{-1}$ above $S_1$ origin is lost at an anomalously rapid rate. As the energy increases from the $S_1$ state to the $S_2$ state, the intersystem crossing rate remains the same, however, the nonradiative decay rate increases rapidly and it becomes the dominant channel for the decay of the $S_2$ state. The lifetime of $S_2$ becomes as short as a few picoseconds.

![FIG. 8. Product growths and disklike image intensity decay as a function of pump probe delay time for $d_5$-pyridine at 193 nm. The wavelength of the VUV laser is 118.2 nm.](image)

![FIG. 9. Photofragment ion images from the photodissociation of 2,6-$d_2$-pyridine at 193 nm. The wavelength of the VUV laser is 118.2 nm.](image)

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same dissociation rate was obtained from the decays of the disklike images as well as from the growths of various dissociation products. This indicates that reactions (2)–(7) all occur in the same electronic state. The fragment transnational energy distributions of the reactions \( \text{C}_4\text{NH}_3 \rightarrow \text{C}_4\text{NH} + \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{NH}_5 \rightarrow \text{C}_2\text{H}_4 + \text{HCN} \) show that the maximum transnational energies reach the maximum available energies of these reactions. Since the maximum transnational energy corresponds to the products produced in the ground electronic state and the ground states of these closed-shell fragments only correlate to the ground state of the parent molecule, the dissociation must occur in the ground electronic state.

### A. Comparison to \textit{ab initio} calculations

We used \textit{ab initio} methods to calculate geometries and energies of various isomers, transition states, and dissociation products in the ground electronic state. In the calculation, the geometries were optimized at the hybrid density-functional B3LYP/6-31G* level\(^{37}\) and the energies were calculated using G3 model chemistry scheme.\(^{38}\) More than 100 of isomers, transition states, and dissociation products have been calculated. In addition, Rice-Ramsperger-Kassel-Marcus (RRKM) calculations of energy-dependent reaction-rate constants were performed for most relevant isomerization and dissociation processes. Only the important isomerization and dissociation mechanisms related directly to the reactions (2)–(7) are described here. The potential-energy diagrams reported in this work are significantly simplified so that only the important intermediates and the highest isomerization barrier in each channel are shown. Detailed calculation results will be presented in another paper.

#### 1. H and D atom exchange

Various isotope-substituted fragments we observed in the photodissociation of 2,6-\(d_2\)-pyridine suggest that H and D atoms exchange before dissociation occurs. H and D atom scrambling can occur from the H and D atom migration along the aromatic ring. The isomerization barriers are in the range of 84–140 kcal/mol, depending on the relative positions of the N atom and the migrating H atom. The H atom migrations with barrier heights below 100 kcal/mol are shown in Fig. 10(a). Some of the other H atom migration processes that have larger barrier heights are shown in subsequent figures along with the relevant dissociation channels. The H and D atom exchange can also be achieved through ring permutation isomerization.\(^{39-41}\) However, as shown in Fig. 10(b), the barriers of ring permutation in the ground electronic state are in general higher than those of H/D atom migration along the aromatic ring. Although one of the ring permutation pathways (I), has a barrier of only 94 kcal/mol, this particular rearrangement does not result in the H-to-D atom exchange in 2,6-\(d_2\)-pyridine. As a result, H and D atom scrambling should mainly come from the H and D atom migration along the aromatic ring. The contribution from the ring permutation isomerization in the ground state is expected to be small.

#### 2. H atom elimination and \(\text{C}_2\text{NH}_5 \rightarrow \text{CH}_2\text{CN} + \text{CH}_2\text{CCH}\)

Except for the H atom elimination channels which result directly from the C–H bond cleavage in pyridine, as shown in Fig. 10(a), all the other ring opening dissociation channels require extensive isomerization processes to occur before the molecule dissociates into two fragments. For reaction (6a), fragments with the structures of \(\text{CH}_2\text{CN}\) (cyanomethyl radical) + \(\text{CH}_2\text{CCH}\) (propargyl radical) have the lowest heat of reaction (110 kcal/mol). The other fragment structures, such as \(\text{CH}_2\text{NC} + \text{CH}_2\text{CCH}\), \(\text{CHCNH} + \text{CH}_2\text{CCH}\), and \(\text{CH}_2\text{CN} + \text{c-C}_3\text{H}_4\) (cyclopropenyl radical), have heats of reaction of 131, 141, and 141 kcal/mol, respectively. These values are so high that these fragments are not likely to be produced. Therefore, we only calculated the dissociation pathways that lead to \(\text{CH}_2\text{CN} + \text{CH}_2\text{CCH}\). There are several dissociation mechanisms to generate these fragments. A simplified energy diagram is shown in Fig. 11. In general, the dissociation starts from the H atom migration along the aromatic ring. This is followed by the ring opening isomerization leading to isomers with a chain structure. Then, H atoms migrate along the chain before the molecule dissociates into two fragments. Two major kinds of barriers can be found on dissociation pathways. One corresponds to H atom migrations along the aromatic ring and the barriers...
are in the range from 91 to 121 kcal/mol. The other is ring opening isomerizations, for which the barriers vary between 104 and 119 kcal/mol.

3. \( \text{C}_5\text{NH}_3 \rightarrow \text{C}_4\text{NH}_2 + \text{CH}_3 \)

The heats of reaction for the formation of methyl radical and \( \text{C}_4\text{NH}_2 \) with the chain structures of \( \text{H}_2\text{CCCCN} \), \( \text{HCCCCNC} \), and \( \text{HCCCHNC} \) are 114.3, 113.8, 136.5 and 136.9 kcal/mol, respectively. The first two structures are most likely to be produced due to their relatively low endothermicities. The isomerization barriers along the two dissociation channels leading to them are as low as 103 and 98 kcal/mol, respectively, as shown in Fig. 12. The dissociation is preceded by complicated isomerization processes. It starts from the generation of chain structure iso- mers, and then H atoms migrate along the chain before the fragmentation occurs. It is interesting to note that the heats of reaction for the generation of various cyclic structures of \( \text{C}_4\text{NH}_2 \) (>180 kcal/mol) are all much larger than the 193-nm photon energy. This result is in contrast to the previous report,\(^{17}\) in which \( \text{C}_4\text{NH}_2 \) was assumed to have a cyclic geometry.

4. \( \text{C}_4\text{NH}_2 \rightarrow \text{C}_3\text{H}_4 + \text{HCN} \)

There are totally five different fragment structures in the HCN elimination channel. The heats of reaction are all much lower than the photon energy. The configurations of the heavy fragment in this channel include cyclobutadiene, \( \text{H}_2\text{CCHCCH} \) (1-buten-3-yn), \( \text{C}_3\text{H}_2 = \text{CH}_2 \) (methyleneacycloprenone), \( \text{H}_2\text{CCCCCH}_2 \) (1,2,3-butatriene), and bicyclo[1.1.0]but-1(3)-ene. For all of these fragments, dissociation barrier heights are found to be lower than the photon energy. A simplified potential-energy diagram of the transition states and intermediates is shown in Fig. 13. The generation of 1,2,3-butatriene is not very likely since the barrier height (125 kcal/mol) is much higher than those for the other channels. Also, according to the experimental observation, the translational energy has a maximum probability at 30 kcal/mol, and the energy as large as 60 kcal/mol can be released. The generation of cyclobutadiene and bicyclo[1.1.0]but-1(3)-ene cannot be the major channel due to the small reverse barrier height at the exit transition states. Therefore, we can conclude that the most likely products are 1-buten-3-yn and methylenecycloprenone.

5. \( \text{C}_5\text{NH}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_3\text{C}_3\text{N} \)

For reaction (5), fragments can only be generated with the structures of HCCCN (propiolonitrile)+\( \text{C}_2\text{H}_2 \) (ethylene), and the heat of reaction is as low as 65.3 kcal/mol. The heavy fragment identified as propiolonitrile can be confirmed from the fact that this fragment was only observed at VUV wavelength of 88.6 nm, but not at 118.2 nm. This is because the ionization energy of propiolonitrile (11.4 eV) is located between the photon energies of these two VUV wavelengths. The dissociation starts from the H atom migration along the aromatic ring, followed by the ring opening isomerization to a chain structure, and then by H atom migration along the chain before dissociation. As shown in Fig. 14, there are two different dissociation mechanisms leading to the same final products. This channel has not been reported in previous studies.

6. \( \text{C}_5\text{NH}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_3\text{C}_3\text{N} \)

The \( \text{C}_2\text{H}_2 \) elimination channel can lead to two possible heavy-fragment structures. One is NCCCH\(_2\) and the other is CNCHCH\(_2\). The heats of reaction for these two structures are 63 and 85 kcal/mol, respectively, and the barrier heights are about the same for both pathways, in the range of 118–120 kcal/mol, as shown in Fig. 15. This channel also has not been reported previously.

7. \( \text{C}_3\text{NH}_5 \rightarrow \text{C}_3\text{NH}_3 + \text{H}_2 \)

In addition to the dissociation channels described above, it is interesting to note that \( \text{H}_2 \) elimination is also energeti-
cally open. As illustrated in Fig. 16, the calculations show that the elimination starts from the H atom migration along the six-membered ring, which is then followed by the three-center H₂ elimination. Barrier heights and heats of reaction are in the range of 110–121 and 85–100 kcal/mol for these two steps, respectively, depending on the relative positions of the N atom and the eliminating H₂ molecules. The dissociation mechanism is similar to that for the H₂ elimination channel from benzene. However, this channel was not observed experimentally. The RRKM calculation suggests that the dissociation rate for H₂ loss is very slow and the branching ratio is small and can be neglected. This is consistent with our observation.

8. Isomerization in the excited electronic state

Although the experimental data suggest that dissociation occurs in the ground electronic state, it is possible that pyridine in the excited electronic state changes its structure before internal conversion into the ground state. One of the possible structural changes is the ring permutation, which is one of the most important isomerizations of aromatic molecules in the S₁ state in the condensed phase. The other possible change in the electronically excited state is the isomerization to the diradical structure. The generation of the diradical structure in the S₁ state has been proposed by Lobastov et al. Since pyridine in this study was excited to a higher-energy level than the S₁ state, internal conversion must be very fast due to a large density of states. These isomerizations are therefore expected to be less important here than in the S₁ state. Even if these isomerizations do occur, our calculations show that in the ground state the barrier heights for the isomerization back to the structure of pyridine are all very small [see Figs. 10(b) and 17]. Therefore, most of the isomers, which could be produced in the excited electronic state, should quickly isomerize to pyridine after internal conversion, and the dissociation again starts from the hot pyridine. Some diradical isomers may dissociate to the C₄H₄ + HCN fragments, however, they cannot contribute to the other dissociation channels. As a result, isomerizations in the excited electronic state are not expected to be important for the pyridine dissociation mechanism at 193 nm.

B. Comparison to photodissociation of benzene

Benzene and pyridine have similar structures. Since the photolysis and photochemistry processes of benzene have been studied extensively, it is thus interesting to compare the photodissociation of pyridine to that of benzene. It has been found that the fluorescence quantum yield of benzene in the S₁ state decreases rapidly when the excitation wavelength is shorter than 244.5 nm. This was interpreted as resulting from a nonradiative pathway, called channel three, by which vibrational energy in excess of ∼3000 cm⁻¹ is lost at an
anomalously rapid rate. The decay rate of benzene after excitation to the $S_1$ state has been measured below and above the channel-three threshold of 244.5 nm under collision-free condition. As a result of these experiments, it can be concluded that the lifetimes are in nanosecond and picosecond ranges for the decay of singlet $S_1$ below and above the channel-three threshold, respectively. A triplet state produced by intersystem crossing from $S_1$ has a longer lifetime, in the range of several hundred nanoseconds. No dissociation was observed from the absorption of 248-nm photons and the dissociation rate was estimated to be smaller than $3 \times 10^3$ s$^{-1}$.20

Benzene in the $S_2$ state produced by 200-nm excitation was found to exhibit fast internal conversion to the $S_0$ and $S_1$ states with a lifetime of ~40 fs, and the decay of the highly vibrationally excited $S_1$ state produced from this internal conversion occurred within 5–10 ps. Recently, we have measured the dissociation rate of benzene after 193-nm excitation under collision-free condition. Dissociation rates of $10^5$ and $5 \times 10^6$ s$^{-1}$, corresponding to $C_6H_5 +H$, $C_6H_4 +H_2$, $C_4H_4 +C_2H_2$, and $C_4H_2 +C_2H_4$ channels are energetically allowed, while the other radical channels are forbidden due to the high dissociation threshold. The transition states leading to the $C_6H_4 +C_2H_2$ and $C_4H_2 +C_2H_4$ products lie higher in energy than available 148.1-kcal/mol photon energy, therefore, these reactions cannot occur. As a result, theoretical calculations show that H atom elimination is the dominant channel and H$_2$ elimination has a very small branching ratio (~1%). Indeed, only H atom elimination was observed in photodissociation of benzene at 193 nm, and no ring opening dissociation was observed at this wavelength.21

A comparison of benzene with pyridine shows that no dissociation was observed from the excitation of both of them at 248 nm. On the other hand, pyridine exhibits a much richer dissociation dynamics and has a faster dissociation rate at 193 nm. Although the number of atoms in pyridine is less than that in benzene and the dissociation rate of pyridine could be expected to be higher due to the smaller total number of vibrational degrees of freedom, the major difference between pyridine and benzene originates from the large change of heats of reaction and barrier heights for various dissociation channels. Most of the dissociation barrier heights of pyridine are below 120 kcal/mol, some of the ring opening dissociation barrier heights are as low as 106 kcal/mol. As a result, ring opening dissociation channels play a very important role in photodissociation of pyridine at 193 nm.

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