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The collision-free photochemistry of methyl azide at 157 nm: Mechanism and energy release

Alfredo Quinto-Hernandez,1,a) Shih-Huang Lee,2 and Alec M. Wodtke3,4
1National Institute of Technology of Mexico, Calzada Tecnologico 27, Zacatepec, Morelos 62780, Mexico
2National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan
3Institut für Physikalische Chemie, Universität Göttingen, Tamannnstrasse 6, D-37077 Göttingen, Germany
4Max-Planck-Institut für Biophysikalische Chemie, Karl Friedrich-Bonhoeffer-Institut, Am Fassberg 11, 37077 Göttingen, Germany

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Synchrotron radiation VUV-photoionization based photofragment translational spectroscopy was used to identify the primary and secondary photodissociation reactions of methyl azide (CH3N3) at 157 nm under collision-free conditions. Two primary dissociation channels are identified, leading to CH3 + N3 (the radical channel) and CH3N + N2 (the molecular elimination channel). The last channel is the major dissociation pathway, but unlike work at longer photolysis wavelengths, here, the radical channel exclusively produces the higher energy isomer cyclic-N3. Product time-of-flight data for both channels were obtained and compared with earlier work on methyl azide photochemistry at 193 nm based on electron impact ionization, allowing us to estimate a product branching ratio

\[
\frac{\Phi_{\text{CH3} + \text{N3}}}{\Phi_{\text{CH3N} + \text{N2}}} = 2.3\% \pm 0.6\%. 
\]

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INTRODUCTION

The surprising discovery of cyclic-N3 formation in the UV photochemistry of simple azides1,2 provides motivation to extend our understanding of azide photochemistry. Interest in cyclic-N3 derives from the fact that observations of cyclic N-allotropes3,4 are so rare. Moreover, new poly-nitrogen molecules might be produced using cyclic-N3 as a precursor; for example, the formation of Td-N4, tetra-azatetrahedrane5,6 is expected to occur when N(2D) reacts in the presence of cyclic-N3 in a barrierless exothermic recombination reaction. Due to their metastability, these poly-Nitrogen molecules may decompose into environmentally clean N2 with large exergy.7,8 Hence, they are considered a novel class of high energy density materials (HEDM).9 Cyclic-N3 also offers the opportunity to study the effect of the geometric phase on the molecular dynamics.9,10 High resolution IR spectra would be a remarkable test of theoretical methods in the vicinity of conical intersections.

The first experimental report of cyclic-N3 was obtained from studies of the photodissociation dynamics of chlorine azide (CIN3) near 235 nm using the velocity map imaging (VMI) technique.1 This observation stimulated other investigations on CIN3, including photofragment translational spectroscopy (PTS) experiments based on electron impact ionization (EI)2,10,11 and synchrotron radiation VUV-photoionization12,13 as well as extending the range of photolysis wavelengths (234-280 nm) used in additional VMI studies.14 All these experiments were consistent with the theoretical work9,15 and revealed that cyclic-N3 is a primary (collision free) product in the UV photochemistry of CIN3. Other photochemical precursors to cyclic-N3 have also been found. Rydberg H-atom time-of-flight studies of hydrazoic acid (HN3) photolysis suggest cyclic-N3 formation,16,17 and clear evidence is found in the near threshold VUV photoionization-based PTS measurements on methyl azide (CH3N3) photodissociation at 193 nm.18 A complete review is available.19

Due to both its energetics and dynamics, methyl azide is a potentially interesting precursor for cyclic-N3. Cyclic-N3 lies at about 30 kcal/mol higher in energy than the better known linear azide radical and exists behind modest barriers to dissociation (33 kcal/mol) and linearization (32 kcal/mol).9 In any photochemical precursor, higher photolysis energy is needed to produce cyclic-N3, while its dissociation and linearization energies are rather low. The high C–N bond energy in methylazide in comparison to the Cl–N bond energy in chlorine azide leads to lower internal energies in the azide photofragments produced by methylazide photolysis. Furthermore, in contrast to Cl, CH3 has the potential to carry away excess energy as internal energy, potentially stabilizing the fragile cyclic product. It is with these ideas in mind that we began work on methyl azide photochemistry.

Previous work shows that there are two primary photodissociation channels in methyl azide photochemistry,

\[
\begin{align*}
\text{CH3N3} & \rightarrow \text{CH3} + \text{N3}, \quad (1) \\
\text{CH3N3} & \rightarrow \text{CH3N} + \text{N2}, \quad (2)
\end{align*}
\]

where reaction (1) is commonly referred to as the radical channel and reaction (2) as the molecular elimination channel.

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a)Author to whom correspondence should be addressed: alfredo.qh@itzacatepec.edu.mx
An early study on the photolysis of methyl azide at 248 nm revealed products only from the molecular channel. Later, using a 193-nm radiation, a C–N bond cleavage was observed, but due to the use of VUV photoionization based product detection, it was difficult to derive a reliable branching ratio since the relevant photoionization cross sections were not known. More recently, we have observed both reaction pathways in the 193-nm photolysis of CH\(_3\)N\(_3\) using PTS with EI ionization based product detection. As relative EI ionization cross sections are easily estimated, an accurate branching ratio could be derived: CH\(_3\)+N\(_3\) = 1.7% ± 0.4%. Product translational energy distributions derived from the radical channel as well as their angular anisotropy parameters were energetically consistent with the cyclic-N\(_3\) formation. We also identified a cyclic-N\(_3\) formation through inspection of the translational energy release in the secondary dissociation of N\(_3\) radicals.

\[ \text{N}_3 \rightarrow \text{N}_2 + \text{N}(^2\text{D}). \]  

(3)

We concluded that cyclic-N\(_3\) is the main 193-nm photoprodut in reaction (1). Furthermore, it was seen that, as desired, the fraction of cyclic-N\(_3\) that underwent secondary dissociation was reduced in comparison to CIN\(_3\).

The dominant molecular channel [reaction (2)] was complicated by several secondary, collision-free dissociation channels:

\[
\begin{align*}
\text{CH}_3\text{N} & \rightarrow \text{CH}_2\text{NH}, \\
\text{CH}_2\text{NH} & \rightarrow \text{HNC} + \text{H}_2, \\
\text{CH}_2\text{NH} & \rightarrow \text{CH}_2\text{N} + \text{H}, \\
\text{CH}_2\text{N} & \rightarrow \text{HCN} + \text{H}. 
\end{align*}
\]

(4–7)

Despite this complexity, reactions (4–7) were all clearly identified and characterized.

These two studies of CH\(_3\)N\(_3\) clearly show that the branching between reactions (1) and (2) is wavelength dependent. In this work, we extend the previous studies at 248 and 193 nm. Specifically, we report observations of the elementary dissociation pathways and the energy release in methyl azide photodissociation at 157 nm using VUV-photoionization-based PTS experiments. The results are similar to the photodissociation dynamics at 193 nm; however, no linear N\(_3\) was detected at this wavelength whatsoever. This is similar to the results obtained in a photodissociation study of CIN\(_3\) at 157 nm. Our results also allow us to derive a product branching ratio \( \Phi_{\text{CIN}_3} \rightarrow \text{N}_2 = 2.3\% ± 0.6\% \) and \( \Phi_{\text{CIN}_3} \rightarrow \text{N}_3 = 97.7\% ± 0.6\% \).

EXPERIMENTS

The experiments were carried out at the Chemical Dynamics Beamline 21 A of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. A complete description of the apparatus used in this study has been previously published and only the relevant details specific to this experiment are given here. The procedure to synthesize methyl azide has also been reported. A mixture of 10\% CH\(_3\)N\(_3\) in Ne was prepared and stored in a stainless steel container and then used to form a supersonically cooled molecular beam by expanding into vacuum through a pulsed valve (Even-Lavie valve) with a backing pressure entering the source chamber at ~1000 Torr. Cluster formation in the molecular beam was avoided by using a pulsed valve at temperatures slightly above 110 °C. The photofragmentation machine uses a rotating source chamber with a fixed detector. The molecular beam intersected an unpolarized, 157 nm excimer laser beam at right angles. The laser produced a 4–7 mJ/pulse and was shaped (3 × 8 mm\(^2\) cross-section) with a focusing lens so that the short distance was along the time-of-flight (TOF) direction. The laser power was controlled to ensure that the TOF spectra were not the result of multiphoton processes. The neutral photofragments traveled 10.05 cm through two separate differentially pumped chambers prior to ionization by a beam of synchrotron radiation (1-mm spot size), which crossed at a right angle to the TOF axis in an ultrahigh vacuum chamber. The photo-ions were mass-selected by a quadrupole mass filter (QMF) before reaching a Daly-style detector for ion counting. The ion flight-times (from the ion source to the Daly detector) were determined independently and could be modeled with a simple formula, \( t_i = \alpha \cdot \sqrt{m} \), where \( \alpha = 5.4 \mu \text{s amu}^{-1/2} \).

We measured the TOF spectra at all mass-to-charge ratios (m/z) where product signal could be detected: m/z = +14(N\(_2\), CH\(_2\)), +15(CH\(_3\)), +27(HCN\(_2\), HNC\(_3\)), +28(N\(_2\), CH\(_2\)N\(_3\)), +29(CH\(_3\)N\(_2\)), CH\(_2\)NH\(_3\)), and +42(N\(_3\)) at laboratory angles, \( \theta_{\text{lab}} = 20°–60° \), in steps of 10°. Each TOF spectrum was averaged over a large number (3000–300 000) of laser shots.

We carried out experiments at various photoionization energies (6.3 < h\(v_{\text{synch}}\) < 16.8 eV) by changing the gap of the U9 undulator. The synchrotron photon energy spread exhibited a ~4% full width at half maximum (FWHM). Higher undulator harmonics were suppressed by an inert gas (Kr, Ne, or Ar) in a gas cell in a design similar to that described by Suits et al. In a separate set of experiments, we recorded the TOF spectra for m/z = +28 and m/z = +42 fragments in the energy ranges of 6.3–16.8 eV and 9.2–12.2 eV, respectively, in 0.20 eV steps at \( \theta_{\text{lab}} = 40° \) or 60°. The photo-fragments detected at m/z = +42 allowed us to measure the photoionization threshold for cyclic-N\(_3\). The ion signal in each experiment was normalized to the laser power and the number of laser shots. The VUV intensity remained constant during all the experiments.

A forward convolution fitting approach was performed to analyze our data. We used the computer program PHOTTRAN to analyze primary dissociations and the program ANAL-MAX to model secondary dissociation. Both programs simulate the TOF spectra based on a user input center-of-mass translational energy distribution, P(E\(_{\text{lab}}\)), which is adjusted iteratively until a satisfactory fit to the experimental data is obtained. For all our data analysis, an anisotropy parameter \( \beta = 0 \) was employed, which corresponds to an isotropic distribution due to the use of unpolarized light during the photolysis experiments.

RESULTS

Although mechanistically complex, the various photochemical channels of methyl azide are easily disentangled...
TABLE I. Observed ion signals and their assignments to specific photochemical channels.

| m/z | Ion/neutral | Primary channel | Secondary channel | $h\nu_{synch}$ (eV)
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>N$/\bar{N}$</td>
<td>(1)$^a$</td>
<td>(3)</td>
<td>12.6</td>
</tr>
<tr>
<td>14</td>
<td>CH$_3^+/\bar{CH}_3$</td>
<td>(1)</td>
<td>NA</td>
<td>11.7</td>
</tr>
<tr>
<td>15</td>
<td>CH$_3^+/\bar{CH}_3$</td>
<td>(1)</td>
<td>NA</td>
<td>10.8</td>
</tr>
<tr>
<td>27</td>
<td>HNC$/\bar{HNC}$</td>
<td>(2)</td>
<td>(5)</td>
<td>15.1</td>
</tr>
<tr>
<td>27</td>
<td>HCN$/\bar{HCN}$</td>
<td>(2)</td>
<td>(4)-(6)-(7)</td>
<td>15.1</td>
</tr>
<tr>
<td>28</td>
<td>CH$_3^+/\bar{CH}_3$</td>
<td>(2)</td>
<td>NA</td>
<td>7.0–16.8</td>
</tr>
<tr>
<td>28</td>
<td>CH$_2^+/\bar{CH}_2$</td>
<td>(2)</td>
<td>(6)</td>
<td>11.3–16.8</td>
</tr>
<tr>
<td>28</td>
<td>N$_2^+/\bar{N}_2$</td>
<td>(1)</td>
<td>(3)</td>
<td>15.7–16.8</td>
</tr>
<tr>
<td>28</td>
<td>N$_2^+/\bar{N}_2$</td>
<td>(2)</td>
<td>NA</td>
<td>15.7–16.8</td>
</tr>
<tr>
<td>29</td>
<td>CH$_3$NH$/\bar{CH}_3$NH</td>
<td>(2)</td>
<td>NA</td>
<td>13.1</td>
</tr>
<tr>
<td>42</td>
<td>N$_3^+/\bar{N}_3$</td>
<td>(1)</td>
<td>NA</td>
<td>11.7</td>
</tr>
</tbody>
</table>

$^a$Observed mass to charge ratio.

$^b$Detected ion and the neutral from which it originated.

$^c$h-ν$_{synch}$ Synchrotron radiation tuned considering the ionization energy of the fragment analyzed.

$^d$See text for an explanation of the reaction channel number.

signal to its neutral photofragment. The various PTS experiments carried out in this work are summarized in Table I. The results allow us to unambiguously determine the collision-free photochemical decomposition mechanism—reactions (1)–(7) above.

TOF data are described in detail now. Figures 1(a)–1(c) show the TOF spectra of m/z = +15(CH$_3^+$) at $h\nu_{synch} = 10.8$ eV and Figs. 1(d)–1(f) show m/z = +42(N$_3^+$) at $h\nu_{synch} = 11.7$ eV. The data are represented by open circles. The solid lines are fits to the data, which are derived from the photochemical mechanism and derived energy release functions and will be described later. Both measured fragments can be attributed to the radical channel, reaction (1). The blue curves in these figures indicate momentum matched products. The red curve in Figs. 1(a)–1(c) come from methyl radicals whose momentum matched the N$_3$ photofragments decomposed before detection.

Secondary dissociation of N$_3$—reaction (3)—was observed in the TOF spectra at m/z = +14(N$_3^+$) and m/z = +28(N$_2^+$). The TOF spectra of m/z = +14 at 12.6 eV—Figs. 2(a) and 2(b)—show a single peak, which is associated with the N-atom formation in reaction (3). Surprisingly, we also observe the TOF signal at $h\nu_{synch} = 11.7$ eV—Figs. 2(c) and 2(d). We attribute this minor signal to CH$_4^+$ formed via dissociative ionization from highly internally excited CH$_3$ fragments, as will be further explained below. Molecular nitrogen produced in reactions (2) and (3) was observed at m/z = +28 TOF spectra with $h\nu_{synch} = 16.5$ eV — Figs. 3(a)–3(c). These spectra also exhibit other contributions to the m/z = +28 signal, indicating that species other than N$_2$ are present. In light of this, we investigated processes resulting from reactions (1)
FIG. 3. TOF spectra of m/z = +28 (a)-(c) and m/z = +29 (d)-(f) at laboratory detection angles, Θ_{lab} = 30°–50°, in steps of 10°. The experimental data are shown as open circles. The brown lines represent the contributions from the molecular elimination channel [reaction (2)]. These were obtained from PHOTRAN and created using the primary P_{CH3N}(E_T) distribution shown in Fig. 9. In the m/z = +28 TOF spectra, the purple and light blue lines represent the contribution of the dissociative ionization CH$_2$NH$^+ \rightarrow$CH$_2$N$^+$ + H [reaction (14)] and the secondary dissociation channel [reaction (6)] from CH$_3$N fragments momentum matched to N$_2$ molecules [reaction (2)], respectively to the total signal. Both fits were also obtained using the total P(E_T) translational energy distribution of CH$_3$N (Fig. 9) as the primary energy release and translational energy distributions with a secondary energy release near zero kcal/mol [Figs. 10(a) and 10(b)]. The pink lines represent secondary dissociation resulting from the N$_3$ molecules, N$_3 \rightarrow$N$_2$+N(2D), formed after C–N rupture [reaction (1)]. This fit emerged using the secondary P_N(E_{2T}) distribution given in Fig. 8. The solid purple, light blue, and pink lines in the experimental data were constructed using ANALMAX.

Identification of these m/z = +28 fragments was carried out collecting the TOF data in the range of photon energies: 6.3–16.8 eV, at Θ_{lab} = 40°. See the supplementary material. This energy range was chosen by considering the ionization energies (IEs) of HCNH (IE = 7.0 eV$^{28}$), H$_2$CN (IE = 10.43 eV$^{29}$, 10.8 eV$^{28}$), and N$_2$ (IE = 15.581 eV$^{30}$). As expected, the m/z = +28 TOF data recorded showed a strong dependence on hν$_{synch}$. For example, at lower energies (hν$_{synch} = 7.0–10.4$ eV) we found a single peak centered at 33 µs (Fig. S1 of the supplementary material) in contrast to the signal at hν$_{synch} = 11.3–14.9$ eV, more intense and evidently with a late contribution (Fig. S2). Such a contribution remains detected at higher photoionization energies (hν$_{synch} = 15.7–16.8$ eV), even when the signal recorded showed a dramatic increase (Fig. S3).

FIG. 4. TOF spectra of m/z = +27 with 15.1 eV ionization photons and laboratory detection angles, Θ_{lab}, of (a) 20°, (b) 30°, and (c) 40°. The experimental data are shown as open circles. In all spectra, the solid magenta lines are the fit from ANALMAX program using the translational energy distribution shown in Fig. 10(c).

For m/z = +29 (CH$_3$N$^+$, CH$_2$NH$^+$), TOF spectra were obtained at hν$_{synch} = 13.1$ eV (Figs. 3(d)–3(f)), resulting from the primary dissociation in the molecular elimination channel [reaction (2)]. At 13.1 eV, only a single peak is detected at arrival times ~21–23 µs.

Finally, m/z = +27 (HCN$^+$, HNC$^+$) TOF spectra were recorded at hν$_{synch} = 15.1$ eV (Figs. 4(a)–4(c)). They comprise a single peak at arrival times ~23 µs and are comparable to those detected in our previous works.$^{18,21}$ Analysis of all these spectra is considered extensively in the section titled “Discussion.”

DISCUSSION

The energetics—zero-Kelvin enthalpies—for all possible photodissociation products of CH$_3$N$_3$ at 157 nm are shown in Fig. 5.$^{9,31}$ This diagram will be helpful to interpret the translational energy distributions P(E_T), obtained from fits to the TOF data. The horizontal dashed black line indicates...
FIG. 5. Energy diagram for the primary and secondary dissociation pathways of methyl azide (CH$_3$N$_3$), constructed from Refs. 9 and 31. The dissociation pathways associated with the CH$_3$ + N$_3$ channel are shown as blue lines: those to the CH$_3$N + N$_2$ channel are presented as green (CH$_3$NH dissociation pathways), brown (CH$_3$N$_2$ isomers), and black lines (CH$_3$N$_3$ isomers). “hv” on the solid vertical arrow indicates a single 157-nm photon (182.1 kcal/mol).

the available energy when methyl azide absorbs a single 157 nm photon. This section is organized as follows. First, an analysis of the primary and secondary photodissociation processes of the radical channel [reaction (1)] involving the fragments m/z = +15, +42, +28, and +14 is offered. Here, we show evidence of photoproduction of cyclic-N$_3$. Next, we discuss the results concerning the molecular channel [reaction (2)] and its subsequent dissociation pathways using data obtained at m/z = +29, +28, and +27. In this channel, several species were identified, including CH$_2$NH, CH$_3$N, HCN, and HNC.

The radical channel, CH$_3$ + N$_3$, and observation of cyclic-N$_3$

The center-of-mass (COM) translational energy distributions, referred to as P(E$_T$), are derived from experimental TOF spectra. Without secondary dissociation of the primary products, P(E$_T$) can be derived from the TOF of either of the photo-fragments of reaction (1) as their relative velocities are constrained by the conservation of linear momentum.

\[
\Delta H^r(\text{cyclic-N}_3) = h\nu_{\text{photolysis}} + \Delta H^r(\text{CH}_3\text{N}_3) - \Delta H^r(\text{CH}_3) - E_{\text{T,lin}}^{\text{max}}(m/z=+42) \\
= (182.1 + 75.9 - 35.85 \pm 0.07 - 82 \pm 2) \text{ kcal/mol} \\
= 140.15 \pm 2 \text{ kcal/mol}.
\]

Here, values for $\Delta H^r(\text{CH}_3\text{N}_3)$ and $\Delta H^r(\text{CH}_3)$ were obtained from Refs. 33 and 34, respectively. To further confirm this assignment, additional experiments were carried out to determine the dependence of the m/z = +42 signal on $h\nu_{\text{synch}}$. Figure 7 shows the TOF-signal integrated vs $h\nu_{\text{synch}}$, seen as solid blue circles. All the integrated intensities were normalized to the laser power and the number of laser shots. The intersection of the two black lines indicates the IE threshold derived from this work (~10.65 eV) consistent with previous theoretical$^{15}$ and experimental$^{12,18}$ reports.

The sum total of this analysis gives rather strong evidence that cyclic-N$_3$ is the dominant product of reaction (1) at 157 nm. The dynamical reasons for this are not clear. It could be that the potential energy surface involved simply leads more easily to the strongly N–N–N bent configurations needed to produce...
provides an estimation of the IE measured in this experiment at ∼ the ionization energy (IE) of cyclic-N the cyclic structure. Secondary dissociation in the radical channel the analysis of data from this work, which strongly suggests the majority of secondary N the cyclic isomer. An alternative dynamical explanation could involve a higher propensity for linear N₃ to undergo secondary dissociation, compared to the cyclic isomer. We now take up the analysis of data from this work, which strongly suggests that the majority of secondary N₃ dissociation proceeds from the cyclic structure. Secondary dissociation in the radical channel In the following, we discuss the dissociation of energetic N₃ and CH₃ fragments. Our approach is to understand the formation of atomic Nitrogen in reaction (3) using the m/z = +14 TOF data obtained at hν_{synch} = 12.6 eV—Figs. 2(a) and 2(b). This analysis is complicated by the observation of the m/z = +14 signal for hν_{synch} = 11.7 eV [Figs. 2(c) and 2(d)], which cannot result from the N-atom. We first dispose of this minor matter. CH₂ formation

\[ \text{CH}_3 \rightarrow \text{CH}_2 + \text{H} \quad (9) \]

is not energetically accessible under our conditions. However, dissociative ionization of CH₃ is possible, if methyl radicals can be formed with large amounts of internal energy.

\[ \text{CH}_3^+ \rightarrow \text{CH}_2^+ + \text{H}. \quad (10) \]

Usually, tunable VUV-synchrotron photoionization reduces the importance of dissociative ionization. However, when the translational energies of the neutral products are low—large photoproduct internal energy—fragmentation following ionization can occur. The solid green lines of Fig. 2 are fully consistent with the data.

Having accounted for the small contribution of CH₃ dissociative ionization to the m/z = +14 data, we can quickly conclude that at hν_{synch} = 12.6 eV (N²D) atoms are the major product of secondary N₃ dissociation [reaction (3); Figs. 2(a) and 2(b)], since under these energy conditions only this spin-allowed dissociation product of N₃ can be ionized, [IE(N²D)] = 12.15 eV. We fit this secondary dissociation data as in previously reported work. Briefly, one requires two translational energy distributions P(E₁). The first is the P(E₂) for the N₃ molecules that dissociate, P_{N₃}(E₁). This is used together with the COM translational energy release associated with reaction (3), P_{N₃}(E₂T) to calculate the observed laboratory frame TOF spectra (see Fig. 8).

One immediately realizes that the P_{N₃}(E₂T) distribution shows an average translational energy release, \( E_{lT} \sim 8.5 \text{ kcal/mol} \) consistent with the predicted exit barrier (7 kcal/mol)⁹ for cyclic-N₃ dissociation to (N²D) and N₂. This is markedly higher than the analogous barrier for linear N₃ dissociation. It also agrees with the P_{N₃}(E₂T) distribution derived from similar PTS experiments at 193 nm.¹¹ seen as

\[ \text{CH}_3 \rightarrow \text{CH}_2 + \text{H} \quad (9) \]

...
a dashed line in Fig. 8. This result provides additional support to our interpretation that cyclic-N\textsubscript{3} dissociates through a spin-allowed channel.

Following this line of reasoning, an analysis of the N\textsubscript{2} molecules produced in reaction (3) is now required. However, m/z = +28 TOF spectra recorded at different $h\nu_{\text{synch}}$ values [Figs. 3(a)–3(c)] clearly suggest a complex photochemistry involving a number of contributions to the m/z = +28 ion signal.

This leads us to analyze the N\textsubscript{2} products of reaction (3) along with these other contributions. As discussed in the section titled “Molecular elimination channel, CH\textsubscript{3}N + N\textsubscript{2}: Primary dissociation,” our observations indicate the presence of N\textsubscript{2} dissociated from N\textsubscript{3} [reaction (3)] and from the molecular channel [reaction (2)] along with CH\textsubscript{2}N.

**Molecular elimination channel, CH\textsubscript{3}N + N\textsubscript{2}: Primary dissociation**

Figures 3(d)–3(f) shows the m/z = +29 TOF data obtained when the undulator gap produced photons at $h\nu_{\text{synch}} = 13.1$ eV, thus allowing us to observe species as methanimine [IE(CH\textsubscript{2}NH) = 9.97 eV\textsuperscript{35}]. These TOF spectra are fit using the $P_{\text{CH3N}}(E_T)$ distribution, shown as a solid brown line in Fig. 9. This $P(E_T)$ comprises a single feature with an average translational energy release of $\bar{E}_T = 26$ kcal/mol and a maximum translational energy release $E_{T\text{max}} = 122$ kcal/mol. Taking into account the energy diagram (Fig. 5), we clearly find that the CH\textsubscript{3}N and N\textsubscript{2} fragments are “momentum matched,” and given the small $\bar{E}_T$ for m/z = +29, a rapid isomerization $^1\text{CH}_3\text{N} \rightarrow \text{CH}_2\text{NH}$ [reaction (4)] follows once CH\textsubscript{3}N is formed. This isomerization is attributed to the limited available energy appearing as translation in this fragment, as it has been seen in previous works at 248 nm\textsuperscript{30} and 193 nm\textsuperscript{18,21}.

A simple energetic analysis for the direct formation of methanimine [reaction (11)] can confirm this evidence. Under the current conditions of our experiment,

$$\text{CH}_3\text{N}_3 \rightarrow \text{CH}_2\text{NH} + \text{N}_2 \quad (11)$$

provides 237.1 kcal/mol of available energy, in comparison to 144.4 kcal/mol if reaction (2) is assumed. This implies that the $\bar{E}_T$ represents only 11% of the available energy in reaction (11), whilst for reaction (2), it increases to 18%. The lowest ratio $\bar{E}_T$ clearly suggests that the direct formation of CH\textsubscript{2}NH + N\textsubscript{2} would be rarer than the molecular channel, followed by the isomerization to CH\textsubscript{2}NH. Observations comparable to our results have been reported before and explained through invoking the soft product impulse approximation.\textsuperscript{36}

We also note that the forward convolution fit from PHOTTRAN is not perfect for all the fragments arriving at later times [Figs. 3(d)–3(f)]. We believe this corresponds to a small contribution of vibrationally excited molecules of the $^1\text{CH}_3\text{N}$ or $^1\text{CH}_2\text{NH}$ ionization, not fully resolved by the wavelength dependent photoionization. Also, attempts were carried out to fit possible contributions from reactions involving triplet species, such as $^3\text{CH}_3\text{N}$ and $^3\text{CH}_2\text{NH}$, but we found no evidence to this.

$P_{\text{CH3N}}(E_T)$ distribution was also useful to explain the m/z = +28 TOF data at $h\nu_{\text{synch}} = 16.5$ eV [Figs. 3(a)–3(c)], through creating the identical distribution $P_{\text{N}_2}(E_T)$. Under this condition, photons are capable of ionizing N\textsubscript{2}, thus leading to the exploration of all possible contributions in the molecular elimination channel [reaction (2)]. In Figs. 3(a)–3(c), we note immediately not only that the $P_{\text{N}_2}(E_T)$ distribution produces the largest contribution to the total m/z = +28 signal but also that other species are required to properly fit the data.

**Secondary dissociation in the molecular elimination channel**

We have already stated that the energy diagram in Fig. 5 suggests that a great variety of reaction pathways contribute to the m/z = +28 spectra, as those producing H\textsubscript{2}CN, H\textsubscript{2}NC, HCNH, and N\textsubscript{2} (eliminated through both the radical and molecular channels). To rule out if such species were produced in our experiment, we performed a photoionization energy dependence study of the m/z = +28 TOF signal. We varied the wavelength of the ionization synchrotron radiation in an energy range of 6.3–16.8 eV and recorded the TOF spectra in steps of ~0.2 eV, at a laboratory angle $\Theta_{\text{lab}} = 40^\circ$. A representative set of the fitted TOF spectra for m/z = +28 at $h\nu_{\text{synch}} = 16.5$ eV is presented in Figs. 3(a)–3(c). Here, the fits emerged as a result of monitoring the evolution of the m/z = +28 TOF data in this energy range, as shown in the supplementary material (Figs. S1-S3). In each normalized TOF spectrum, we inspected for contributions, which were then resolved accordingly.

Our analysis of the molecular elimination channel is obscured by the initial observation of the m/z = +28 signal in the range $h\nu_{\text{synch}} = 7.0$–10.4 eV (Fig. S1 of the supplementary material). HCNH, formed from the isomerization of CH\textsubscript{2}N as a tertiary event,

$$\text{CH}_3\text{N} \rightarrow \text{HCNH}, \quad (12)$$

and similarly H\textsubscript{2}NC from HCNH,

$$\text{HCNH} \rightarrow \text{H}_2\text{NC}, \quad (13)$$

cannot be associated with this signal. First, the linear isomer of HCNH is unlikely to undergo a transition from its neutral
ground to its bent ion state due to small FC-factors\(^{29}\) and second, the experimental and theoretical determinations of the ionization energies for trans-HCNH, cis-HCNH, and H\(_2\)NC prevented us to explore the presence of these species here.\(^{29}\) In order to explain the observations in this energy range, we fit our data using the forward convolution simulation provided by ANALMAX, considering the primary \(P_{\text{CH3N}}(E_T)\) distribution (Fig. 9) to characterize the primary reaction [reaction (2)] and a near-zero kinetic energy release distribution [Fig. 10(a)] for a possible secondary dissociation. This result is seen in Fig. S1 as solid purple lines. Given that the CH\(_3\)NH fragments were formed with large internal energies inferred from the limited translational energy release shown in Fig. 9, we believe this observation corresponds to the dissociative ionization

\[
\text{CH}_3\text{NH}^+ \rightarrow \text{CH}_3\text{N}^+ + \text{H} \quad (14)
\]

that remains important at all photoionization energies employed in this experiment, even when typically such a fragmentation is expected to be inhibited.

Recall that the m/z = +28 TOF spectra in \(h\nu_{\text{synch}} = 11.3-14.9\) eV (Fig. S2 of the supplementary material) progressively shows a second contribution at later times. The fast signal is immediately assigned to the CH\(_3\)N\(^+\) formation via reaction (14), by using the same procedure as in \(h\nu_{\text{synch}} = 7.0-10.4\) eV. Here, we easily realize that any additional signal remains unrelated to the N\(_2\) formation, given that the ionizing synchrotron radiation was not sufficient to ionize such molecules. Therefore, a fitting procedure for the slow contribution was carried out considering the CH\(_2\)N\(^+\) formation from neutral methanimine [CH\(_2\)NH, reaction (6)] with H-atom loss, as it has been reported previously.\(^{18,21}\) To fit the data, we use the \(P_{\text{CH3N}}(E_T)\) distribution (Fig. 9) for the primary release and the \(P_{\text{CH2N}}(E_T)\) distribution [shown as solid light blue line in Fig. 10(b)] for the secondary release. As a result, the maximum energy release for the secondary distribution falls to zero at \(\sim 0.06\) kcal/mol, consistent with the formation of CH\(_2\)N through a simple bond rupture with an H-atom release. Given all this, we can clearly distinguish between the daughter ion and the secondary product of CH\(_2\)N in two different ranges of photoionization energy.

An analysis of the TOF data in \(h\nu_{\text{synch}} = 15.7-16.8\) eV is followed now. Here, we estimate contributions of N\(_2\) from reactions (2) \((\text{N}_2 + \text{CH}_3\text{N})\) and (3) \((\text{N}_2 + \text{N}(^{2}\text{D}))\) to the total m/z = +28 signal, by considering those already found from reactions (6) and (14). These contributions are shown as light blue and purple lines in Figs. 3(a)–3(c) and Fig. S3 of the supplementary material, correspondingly. To simulate the contribution from reaction (2), we used the translational energy distribution \(P_{\text{N2}}(E_T)\) into the same TOF data, strongly suggesting that the formation of N\(_2\) is dominant through this molecular channel. Similarly, we simulate the contribution of N\(_2\) secondarily dissociated from N\(_3\) fragments [reaction (3)] using the energy distribution \(P_{\text{N3}}(E_T)\) over the same data (shown as solid pink lines), resulting in a small contribution that is considered to fully resolve the m/z = +28 TOF signal.

Finally, we study the m/z = +27 photofragments, recorded at \(h\nu_{\text{synch}} = 15.1\) eV [Figs. 4(a)–4(c)], in which the presence of HCN (or HNC) \([\text{IE(HCN)} = 11.5\) eV\(^{37}\) (theoretical), \(<12.07\) eV\(^{38}\) (experimental)] and HNC \([\text{IE(HNC)} = 13.0\) eV\(^{37}\) (theoretical), \(13.607 \pm 0.002\) eV\(^{39}\) (experimental)] can be detected. As shown in the energy diagram (Fig. 5), CH\(_3\)NH can produce HCN or HNC having H\(_2\) as a counter-fragment, or after two subsequent H-atom departures, HCN is formed and then isomerized to HNC. We noted the similar shape of the m/z = +27 TOF spectra with those in our previous work\(^ {21}\) in which the signal was attributed to reaction (7) and described as a tertiary process. Consequently, we use ANALMAX to evaluate this possibility, in which the simulated tertiary processes is treated as a secondary step, assuming that a secondary translational energy distribution \(P(E_T)\) provides a maximum near zero. Our best fits (seen as solid magenta lines in Fig. 4) reveal that reaction (7) is the most likely process in our experiment. Such a fitting was created after using the distribution \(P_{\text{CH3N}}(E_T)\) (Fig. 9) for the primary translational energy release and \(P_{\text{HCN}}(E_T)\) [Fig. 10(c)] for the secondary release. The \(P_{\text{HCN}}(E_T)\) distribution obtained shows a maximum secondary energy release of \(\sim 0.35\) kcal/mol,
agreed well with this assumption. The excellent similarity between the experimental results at 197 and 157 nm suggests that the m/z = +27 fragments may have the same energetic origin.

**Branching ratios of detected dissociation channels**

An accurate product branching ratio can be obtained for the radical [reaction (1)] and molecular channels [reaction (2)] if relative photoionization cross-sections are known for the observed products. However, most of these cross-sections have remained undetermined since we carried out our previous experiments using synchrotron radiation. Fortunately, if we compare the TOF signal levels for the nonreactive experiments using synchrotron radiation, we can extract easily a global branching ratio $R$ for CH$_3$ + N$_3$ versus CH$_3$N + N$_2$ within our experimental uncertainty. The global branching ratio was obtained after following an appropriate normalization (VUV intensity, laser power, and the number of laser shots) of the data at a few different laboratory angles ($\Theta_{lab} = 20^\circ$-60$^\circ$), in both the photoionization and electron impact data. In the experiments based on electron impact ionization, the cross sections for the primary products were estimated using additivity rules, resulting in the cross sections of 3.7 x 10$^{-15}$ cm$^2$ for CH$_3$ and 2.6 x 10$^{-16}$ cm$^2$ for N$_2$. Branching ratios for CH$_3$ versus N$_2$ [reaction (2)] for the several laboratory angles considered in this work are presented in Table II, using the photoionization energies of 11.7 eV for CH$_3$ and 16.5 eV for N$_2$. From the table, a global product branching ratio for the C–N and N–N ruptures in CH$_3$N$_3$ of 97.7% (±0.6%) is obtained. Considering that only ~5% of the N$_3$ fragments present in reaction (1) fail to undergo secondary dissociation, we conclude that ~0.12% of these molecules produced during the photolysis of CH$_3$N$_3$ at 157 nm are cyclic-N$_3$.

**CONCLUSION**

Methyl azide (CH$_3$N$_3$) has been photodissociated at 157 nm under collision-free conditions, and the resulting photoproducts (N$_3$, CH$_2$NH, N$_2$, CH$_3$N, HCN/HNC, CH$_3$, and N) have been detected using VUV synchrotron radiation-based photofragment translational spectroscopy. All the evidence obtained suggests exclusive production of the cyclic isomer of N$_3$, in contrast to previous work at other photolysis wavelengths. At 157 nm, the C–N dissociation in CH$_3$N$_3$ that leads to the formation of this isomer is increased by ~35% with respect to the results obtained previously at 193 nm, thus obtaining a branching product ratio of $\Phi_{CH_3N_3}/\Phi_{CH_3N_2} = 2.3\%$ (±0.6%). This work also confirms the important experimental data associated with Cyclic-N$_3$, including its heat of formation and ionization energy.

**SUPPLEMENTARY MATERIAL**

See supplementary material for the m/z = +28 TOF signal in the photon energy range 7.0–16.8 eV.

**ACKNOWLEDGMENTS**

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**TABLE II. Estimated product branching ratio $R$ of CH$_3$ + N$_3$ versus CH$_3$N + N$_2$ for laboratory angles, $\Theta_{lab}$ = 20°-60°.**

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<th>$\Theta_{lab}$</th>
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