Photofragmentation translational spectroscopy was used to identify the primary and secondary reaction pathways in the KrF laser (248 nm) photodissociation of chlorine azide (ClN₃) under collision-free conditions. Both the molecular channel producing NCl⁺ (X³Σ⁺, a¹Δ)+N₂ and the radical channel producing Cl⁺ (²P_g)+N₃ were analyzed in detail. Consistent with previously reported velocity map ion imaging experiments [N. Hansen and A. M. Wodtke, J. Phys. Chem. A 107, 10608 (2003)] a bimodal translational energy distribution is seen when Cl atoms are monitored at m/z =35(Cl⁺). Momentum-matched N₃ counterfragments can be seen at m/z=42(N₃⁺). The characteristics of the observed radical-channel data reflect the formation of linear azide radical and another high-energy form of N₃ (HEF-N₃) that exhibits many of the characteristics one would expect from cyclic N₃. HEF-N₃ can be directly detected by electron-impact ionization more than 100 μs after its formation. Products of the unimolecular dissociation of HEF-N₃ are observed in the m/z =14(N⁺) and m/z=28(N₂⁺) data. Anisotropy parameters were determined for the primary channels to be β=−0.3 for the NCl forming channel and β=1.7 and β=0.4 for the linear N₃ and HEF-N₃ forming channels, respectively. There is additional evidence for secondary photodissociation of N₃ and of NCl. © 2005 American Institute of Physics. [DOI: 10.1063/1.1948381]

INTRODUCTION

This paper springs from our continuing interest in the rich UV photodissociation dynamics of chlorine azide (ClN₃). Primary photoproducts are formed in a molecular elimination channel,

\[ \text{ClN}_3 + h\nu \rightarrow \text{NCl}(a^1\Delta) + \text{N}_2(X^1\Sigma^+) \]  

(1a)

or in a radical-forming bond-rupture channel

\[ \text{ClN}_3 + h\nu \rightarrow \text{Cl}(^2P_g) + \text{N}_3(X^2\Pi) \]  

(2a)

Historically, interest in the photochemistry of ClN₃ (Refs. 6–13) derived from the utility of one of its photoproducts, NCl(a¹Δ), as an effective energy carrier in an all gas-phase chemical iodine laser (AGIL).12,14–18

More recently, the ClN₃ photochemistry has received considerable attention due to its potential use as a possible photolytic precursor of cyclic N₃. Hansen and Wodtke reported velocity map ion imaging experiments of ClN₃ photodissociation at 235 nm under collision-free conditions and showed that the translational energy distribution of the Cl fragment is bimodal.1 This observation indicates that, in addition to the formation of the well-known linear N₃ (azide radical), the radical channel also leads to the formation of a high-energy form of the N₃ molecule hereafter referred to as HEF-N₃. It was pointed out that the maximum translational energy release of reaction,

\[ \text{ClN}_3 + h\nu \rightarrow \text{Cl}(^2P_g) + \text{HEF-N}_3, \]  

(2b)

could be used to extract a heat of formation that was in excellent agreement with theoretical predictions of the heat of formation of the cyclic-N₃ isomer.

Although it is yet to be definitively proven that cyclic N₃ is a primary product of ClN₃ photochemistry, its predicted properties are quite interesting and represent a significant motivation for the present study. Briefly, cyclic N₃ is a Jahn–Teller molecule that exhibits a conical intersection at the D₃h (equilateral triangle) configuration. This conical intersection must distort to form one of the three equivalent C₂ᵥ minima. The barrier to interconversion between equivalent C₂ᵥ minima (pseudorotation) is comparable to the zero-point vibrational energy. The vibrationless state of N₃ is doubly degenerate, delocalized between minima, and lies ~9 kcal/mol below the conical intersection.19 A recent paper20 has shown that cyclic N₃ is ideal for the study of the geometric phase effect21,22 (Berry’s phase) in molecules. The geometric phase
effect introduces “correction” factors in determining the energies of the vibrational states in this molecule, which are predicted to be on the order of $10^5$ cm$^{-1}$. Furthermore, without correct consideration of the geometric phase effect, one cannot obtain accurate vibrational wave functions. Even the correct symmetry of the ground vibrational state ($E$) is incorrectly predicted to be $A_j$ if Berry’s phase is neglected.\textsuperscript{20} Experimental studies on the spectroscopy of cyclic $N_3$ would be very useful in extending our understanding of these phenomena in molecular systems.

What we know about HEF-$N_3$ has been learned from a few experiments and comparisons to theoretical work on cyclic-$N_3$.\textsuperscript{1,4,5,19,20,23–25} The experimentally observed excitation energy $\Delta E=31\pm2$ kcal/mol is in very good agreement with recent \textit{ab initio} calculations, which predicted the existence of a stable cyclic-$N_3$ isomer at an energy of 30.0 kcal/mol above the energy of the linear-$N_3$ isomer.\textsuperscript{1,23} Recently, Samartzis \textit{et al.} observed distinct ionization thresholds for the two forms of $N_3$.\textsuperscript{5} Their experimental value IP (HEF-$N_3$) $=10.7\pm0.2$ eV agrees well with the theoretically predicted value for cyclic $N_3$ of 10.58 eV.\textsuperscript{24}

Babikov \textit{et al.} presented a sophisticated adiabatic ground electronic state potential-energy surface which is constructed based on extensive high-level \textit{ab initio} calculations.\textsuperscript{19} Theory shows that cyclic $N_3$ is metastable with respect to the spin-forbidden dissociation,\textsuperscript{19,25}

$$\text{cyclic } N_3(2B_j) \rightarrow N(5S) + N_2(X^{1\Sigma_g^-})$$

$$\Delta E \sim -32.3 \text{ kcal/mol.} \quad (3)$$

In addition, it is known that the doublet-quartet surface crossings that, when traversed, lead to dissociation lie about 28 kcal/mol above the cyclic-$N_3$ minimum.\textsuperscript{25} Thus, while cyclic $N_3$ is metastable, it is thought to be long lived and, as it carries a great deal of chemical energy, it is an excellent new candidate for technological applications in energy storage, high nitrogen explosives, and clean propellants.

Other experiments have provided essential information needed to evaluate the photochemistry of $\text{ClN}_3$. Velocity map ion imaging of $\text{ClN}_3$ photoproducts was used to investigate the dissociative photoionization of $\text{ClN}_3$ under collision-free conditions,

$$\text{ClN}_3 + 2h\nu \rightarrow \text{ClN}_3^+ + e^- \rightarrow \text{NCl}^+ + N_2(X^{1\Sigma_g^+}) + e^-,$$

(4)

which was observed by recording velocity map images of NCl$^+$ as well as state-selected N$_2$.\textsuperscript{3} In another experiment, the molecular channel (1) was observed via velocity map images of state-selected N$_2$.\textsuperscript{2} These two pieces of work provided accurate thermochemistry for reaction (1): $\Delta E = +4.8 \pm 1.8$ and $-21.4 \pm 2.1$ kcal/mol for the decomposition of $\text{ClN}_3$ into N$_2(X^{1\Sigma_g^+}) + \text{NCl}(a^1\Delta)$ and NCI($X^{3\Sigma}$), respectively. A comprehensive reevaluation of the thermochemistry of all molecules containing a single Cl atom and three N atoms including all new data from velocity map imaging has been reported.\textsuperscript{1} All of the above experiments agree well with literature values for the 0 K heats of formation of N$_2(X^{1\Sigma_g})$ and ClN$_3$.\textsuperscript{26–28} The known dissociation energies of Cl–N$_3$ and of NCI ($a^1\Delta,X^{3\Sigma}$) are also in agreement with the new experiments.\textsuperscript{29,30} All derived thermodynamic results were presented in Ref. 1 and will be helpful in the analysis of this work. Figure 1 summarizes the derived energy levels of the Cl–N–N–N system and shows the calculated barriers for dissociation of linear and cyclic $N_3$ into $N_2 + N + Cl$.11 As in the earlier imaging experiments,\textsuperscript{3} a bimodal translational energy distribution was reported for the Cl atom in the PTS experiment.

In this paper, we describe a thorough analysis of the PTS experiments. In addition to the Cl and NCI data which were partially discussed in the previous letter, we now include data from $N_3$ photofragments as well as from $N_2$ and N fragments formed in secondary dissociation reactions. We show that HEF-$N_3$ can be detected by EI more than 100 µs after its formation. Specifically, we see that the $N_3$ photofragments exhibit a bimodal translational energy distribution that is consistent with momentum-matched Cl photofragments and the results from velocity map imaging. In addition, the angular distribution of the fast $N_3$ (linear azide) matches that of the fast Cl. Likewise, the angular distribution of the HEF-$N_3$ matches that of the slow Cl. A complete analysis of second-
ary dissociation pathways was carried out. This analysis shows that HEF-N$_3$ undergoes unimolecular dissociation forming both N($^3D$)+N$_2$ and N($^4S$)+N$_2$. In addition, secondary photodissociation of N$_3$ is seen, as is secondary photodissociation of NCI. We also conclude that unimolecular decomposition of energized NCI can be ruled out as a source of the slow Cl fragments.

Overall, these experiments now reveal the full set of microscopic collision-free decomposition pathways of ClN$_3$ resulting from photodissociation at 248 nm. The results provide a much firmer footing for the analysis of ClN$_3$ photolysis and add weight to previous conclusions concerning the possible photolytic production of cyclic N$_3$.

**EXPERIMENT**

The molecular-beam photodissociation instrument on which these experiments were performed has been described in detail previously.$^{31,32}$ A mixture of ClN$_3$ seeded in He carrier gas was prepared by passing a mixture of 10% Cl$_2$ in He over moist sodium azide (NaN$_3$). The NaN$_3$ was suspended in cotton wool and excess water was removed by passing the mixture through a drying agent (Drierite). Under normal operating conditions, mass spectral analysis of the beam showed NCl$^+$, an ionizer-induced fragment of ClN$_3$$^+$, and little or no Cl$_2$$^+$. When Cl$_2$$^+$ signal could be detected, the NaN$_3$ sample was replaced.

Using a backing pressure of ~0.5 bar, a pulsed molecular beam was formed by expanding the ClN$_3$/He mixture into vacuum through a piezoelectrically actuated pulsed valve.$^{33}$ After passing through two collimating skimmers, the molecular beam intersected a 28 ns pulsed beam of unpolarized 248 nm laser light produced by a Lambda Physik KrF excimer laser. Both the valve and the laser were operating at 100 Hz. The laser output (~72 mJ energy/pulse) was focused to a ~10 mm$^2$ spot at the region of intersection.

Photofragments scattered in the plane of the molecular laser beam were detected as a function of laboratory scattering angle, $\Theta$ with a rotatable, triply differentially pumped mass spectrometer. After passing through three collimating apertures, the photofragments were ionized by electron impact, mass selected with a quadrupole mass filter, and detected with a Daly-style detector. At various scattering angles, $\Theta=10^\circ$–$60^\circ$ in $10^\circ$ steps, photofragment time-of-flight (TOF) distributions were taken for ions at selected mass-to-charge ratios, $m/z=35$ (Cl$^+$), 49 (NCI$^+$), 42 (N$_2$), 28 (N$_2$), and 14 (N$^+$), using a multichannel scaler interfaced to a personal computer. The velocity distribution of the parent ClN$_3$ molecular beam was characterized by TOF at $\Theta=0^\circ$ using a retractable slotted chopper wheel to modulate the molecular beam.

TOF spectra obtained in this fashion were fitted by either the PHOTRAN (Ref. 34) or ANALMAX (Ref. 35) forward-convolution program. Both programs simulate the TOF spectrum based on “guessed” center-of-mass translational energy [$P(E_T)$] distributions that are iteratively improved until a satisfactory fit to the data is obtained. Beam velocity, laboratory angle, dissociation and ionization volumes, finite angular acceptance angle of the detector, laser power, and polarization are additional program parameters used in the forward convolution.

**RESULTS AND ANALYSIS**

This section of the paper is organized as follows. First, the results from primary photodissociation processes are discussed. In particular, the analysis of the $m/z=49$ (NCI$^+$) TOF spectra is presented first, showing the energy release of reaction (1). Because the energy distribution of the N$_2$ counterfragments is complicated by secondary unimolecular dissociation and photodissociation processes of N$_3$, its analysis is presented later. In the second stage of presentation, we analyze the radical channel—in particular, the observed translational energy distribution of the Cl fragments. We then move on to an analysis of the $m/z=42$ (N$_2$) TOF, which exhibits the N$_3$ counterfragments to Cl in the radical channel. Finally the secondary processes are presented. Analysis of $m/z=28$ (N$_2^+$) and $m/z=14$ (N$^+$) leads to information on the unimolecular decomposition of N$_3$ and to evidence that the HEF-N$_3$ can be photodissociated at 248 nm. As part of the $m/z=35$ (Cl$^+$) TOF analysis, secondary NCI photodissociation is seen.

**Molecular channel NCI+ N$_2$**

Observed TOF spectra of the NCI fragments ($m/z=49$) originating from reaction (1) are shown in Fig. 2 at several scattering angles, $\Theta$. The data are represented by the open circles, while the solid lines are the results of forward-convolution simulations of the experiment using an optimized center-of-mass translational energy distribution shown in Fig. 3.

The best fit to the experimental data shown in Fig. 2 was obtained using the translational energy distribution shown in Fig. 3 and an anisotropy parameters of $\beta=-0.3$. The derived translational energy distribution shown in Fig. 3 is in good agreement with the previously reported distribution.$^4$ Owing to the non-state-selective detection scheme used in this experiment, identification of the electronic state of the NCI product, i.e., evaluating the relative importance of reactions (1a) and (1b), is not possible, although previous studies provided evidence that the spin-allowed reaction (1a) is more probable than reaction (1b).$^{11}$

Besides reaction (1), other pathways, including the production of NCI ($X^2 \Sigma^+$) via a spin-allowed channel,

$$\text{ClN}_3 + h\nu \rightarrow \text{NCI}(X^2 \Sigma^+) + N_2(A^2 \Sigma_g^+) \tag{5}$$

come into consideration. While this channel is not energetically accessible for 248-nm photolysis, when the photolysis wavelength is 193 nm, N$_2(A^2 \Sigma_g^+)$, presumably from channel $5$, has been detected,$^{6,12}$ along with NCI ($b^1 \Sigma^+$) which can be produced by a second spin-allowed channel.$^{6,36}$

$$\text{ClN}_3 + h\nu \rightarrow \text{NCI}(b^1 \Sigma^+) + N_2(X^1 \Sigma_g^+) \tag{6}$$

Coome$\text{et al.}$ reported that channels (5) and (6) amount to only ~1% of the 193 nm photolysis products.$^{12}$ Komissarov$\text{et al.}$ estimated that ~1% of NCI is formed in the $b^1 \Sigma^+$ state after ClN$_3$ photolysis at $\lambda=248$ nm.$^{11}$ N$_2(A^2 \Sigma_g^+)$ lies ~6.2 eV above the ground-state N$_2(X^1 \Sigma_g^+)$ and therefore is
not accessible by photolysis at $\lambda$=248 nm. Consequently, reactions (5) and (6) are not considered likely candidates to explain the data of Fig. 2.

According to recent experimental and theoretical work, the maximum available translational energy release is $E_{\text{max,NCI}}(a)=108$ kcal/mol and $E_{\text{max,NCI}}(X)=135$ kcal/mol for channels (1a) and (1b), respectively.\(^1,4\) These values are substantially larger than the observed maximum translational energy release of $\sim 48$ kcal/mol (see Fig. 3). This means that the primary products, $N_2$ and NCI, are formed with a considerable amount of internal energy. This strong tendency to channel available energy into internal energy of the fragments has been postulated before on the basis of indirect kinetic evidence\(^3,8\) and it is the most important feature of reaction (1). Indeed more than 70 kcal/mol goes to excite the internal degrees of freedom of the two diatomic products.

**Radical-channel Cl+N$_3$**

**Cl photofragments**

The observed TOF spectra of the Cl fragments at $m/z$ =35 are shown at several scattering angles, $\Theta$, in Figs. 4(a)–4(c). The data are represented by the open circles, while the solid and dashed lines are the results of forward-convolution simulations of the experiment using optimized center-of-mass translational energy distributions shown in Fig. 5.

As has been briefly discussed in the previous letter,\(^4\) we note that a bimodal $P(E_T)$ distribution for the Cl+$N_3$ channel is needed to fit the two dominant peaks in the TOF spectra of Figs. 4(a)–4(c). The individual contributions are shown as dashed (fast channel) and solid lines (slow channel), respectively. The $P(E_T)$ distribution for the Cl data in Fig. 5 is experimentally indistinguishable from that obtained by Hansen and Wodtke in a recent velocity map imaging experiment, in which the faster feature was assigned to the formation of linear $N_3$ and the slower feature was interpreted as possible evidence for the photolytic production of cyclic $N_3$.\(^1\) Thus, the photofragment translational spectroscopy experiment confirms the existence of a bimodal Cl-atom translational energy distribution in the radical channel. The anisotropy parameters are determined to be $\beta=1.75(10)$ and $\beta=0.35(5)$ for the fast and slow channels, respectively. Those values compare well with those determined by velocity map imaging ($\beta=1.70(5)$ and $\beta=0.39(1)$).\(^1\) The branching ratio between the two channels is fast Cl/slow Cl $\sim 0.75/0.25$. Using the velocity map imaging technique a similar branching ratio of $0.8/0.2$ was found.\(^1\) The $P(E_T)$ distribution shown in Ref. 4 exhibiting more of the slow channel is incorrect.

A closer look at the TOF spectra of the Cl product in Fig. 4 indicates a small contribution from very fast photofragments. This feature is most obvious at larger scattering angles and it is shown as dotted curve enlarged in the inset of Fig. 4(c) for the $\Theta=50^\circ$ data. This feature results from secondary photodissociation of NCI at 248 nm:

$$\text{NCI}(X^2S, a^1\Delta) + h\nu \rightarrow \text{N}^4S, ^2D + \text{Cl}(^2P).$$ (7)

The derived $P(E_T)$ for the secondary photodissociation of NCI peaks at 80 kcal/mol and exhibits a half-width of $\sim 10$ kcal/mol. In principle, we can use this information to evaluate the internal energy content of the NCI photodisso-

![FIG. 2. Time-of-flight (TOF) spectra of $m/z$=49(NCl$^+$) at detection angles $\Theta=10^\circ$, 30$^\circ$, and 60$^\circ$. For all spectra the open circles represent the data. The solid line represents the forward-convolution fit to the data using the $P(E_T)$ distribution shown in Fig. 3.](image-url)

![FIG. 3. Center-of-mass translational energy distribution $P(E_T)$ for the molecular channel forming NCI in the ClN$_3$ photodissociation. This energy distribution is used to reproduce the observed spectra in Fig. 2.](image-url)
ciated in this work. In practice, this analysis is ambiguous, as the identities of the reactant and product electronic states in (7) are not known.

N₃ photofragments

The observed TOF spectra of the N₃ counterfragment for radical channel (2) are shown in Figs. 4(d)–4(f). Again, the data are represented by the open circles, the simulations by the dashed (fast channel) and solid (slow channel) lines. As will be discussed below, the strongest peak in the N₃ TOF spectra corresponds to the formation of linear azide. However, a second peak which is much more obvious in the Cl⁺ data is also present.

The N₃ TOF spectra shown in Figs. 4(d)–4(f) were used to derive a center-of-mass translational energy distribution for the radical channel, similar to what was done for the Cl TOF data. The results of this analysis are shown in Fig. 5 and are compared to the P(Eₜ) obtained from the analysis of the Cl data. The derived translational energy distributions match closely above about 26±2 kcal/mol. This suggests that while low-translational energy Cl atoms formed together with HEF-N₃ can easily be detected at the ionizer after about 100 µs, not all of the corresponding HEF-N₃ can. Comparing the intensities of the slow channels in Fig. 5 we conclude that 10% of the HEF-N₃ fragments are actually detected. This could be due to the preferential ion fragmentation possible for highly energized neutrals or to the onset of unimolecular dissociation of the neutral N₃ on a time scale faster than 100 µs. It could also be due to secondary photodissociation of NCl photofragments can be seen, especially in the inlet in (c) as dotted line.

In addition to yielding a P(Eₜ) distribution, the m/z = 42(N⁺₃) TOF data allowed us to determine the anisotropy parameters for the reactions (2a) and (2b) by way of an independent set of data. The derived values of β=1.7(1) and β=0.39(5) for reactions (2a) and (2b), respectively, agree with results obtained by analyzing angular distribution of the Cl fragments by both photofragment translational spectroscopy and velocity map imaging. The correspondence between β parameters and translational energy distributions indicates that both the fast and the slow channel in the Cl data are indeed correlated to the formation of momentum-matched N₃ counterfragments. This shows clearly that besides the linear N₃, HEF-N₃ is formed and can be detected by EI mass spectrometry.
The observed translational energy distributions are quantitatively consistent with the formation of linear N$_3$. The dissociation energy of ClN$_3$ to form Cl and linear N$_3$ is $D_0$(Cl–N$_3$) = 49.1 kcal/mol. If all the available energy is channeled into translational energy, i.e., the products are formed in their ground states, the maximum translational energy release would be 66.1 kcal/mol, using a photon energy of 115 kcal/mol (λ = 248 nm). The observed maximum translational energy release $[E_T^{max}](\text{linear N}_3 + \text{Cl})$ = 66.9±1 kcal/mol is marked in Fig. 5 and agrees well with the predicted value. We therefore assign the fast Cl and N$_3$ fragments to the formation of linear N$_3$ in reaction (2a). This assignment is supported by another experiment by Samartzis et al. who determined the ionization potential of the fast N$_3$ fragments to IP=11.1 eV which can be identified with the well-known IP of linear N$_3$.

For the slow Cl+N$_3$ channel, the maximum observed translational energy release is $E_T^{max}(\text{HEF-N}_3 + \text{Cl})$ = 36.8±2 kcal/mol (see Fig. 5), a value which is derived from the Cl as well as the N$_3$ data. The difference between the maximum translational energy release of the fast and slow channels represents the excitation energy of HEF-N$_3$ with respect to ground-state linear N$_3$. This value (30.1±3 kcal/mol) agrees well with a previous experimentally determined excitation energy (31±2 kcal/mol) obtained from velocity maps of the Cl fragments.

**Secondary dissociation processes: N$_2^+$ and N$^+$ data**

As mentioned above, comparison of the TOF spectra in Fig. 4 and the translational energy distributions in Fig. 5 leads to the conclusion that only 10% of the slow N$_3$ photofragments are detected. Consequently we looked at the TOF spectra for $m/z$=14(N$^+$) and $m/z$=28(N$_2^+$) for evidence of unimolecular and/or photinduced dissociation of N$_3$.

The data are shown in Figs. 6 and 7 for different scattering angles, Θ. The data are represented by the open circles and the simulations which will be discussed in this section are represented by the colored lines. Because of the molecular channel forming N$_2$ being just a minor channel (5±3%) and because of the high background and low S/N experienced (due to background CO in the detector), for $m/z$=28 we were limited to obtaining data at Θ=10° and 30°.

**Dissociative ionization of N$_3$ photofragments**

Figures 6 and 7 show that both the $m/z$=14 and the $m/z$=28 TOF spectra are dominated by a strong peak which, when corrected for differences in ion flight through the quadrupole mass spectrometer, appears at the same TOF as the dominant peak in the $m/z$=42 TOF data, now assigned to the formation of the linear N$_3$(X $^2\Pi$). It is therefore clear that the major peaks in the $m/z$=14(N$^+$) and $m/z$=28(N$_2^+$) data result from dissociative ionization of linear N$_3$ in the ionizer and provide redundant information on reaction (2a). Since EI with electron energies of ~160 eV was used, observing ionizer-induced fragmentation is not surprising. Because it is energetically more favorable and therefore, on the basis of statistical theories of ion dissociation more likely for N$_3^+$ to
dissociate into N$_2$ + N$^+$ rather than into N$_2^+$ + N, this feature is substantially stronger in the m/z=14 than in the m/z=28 TOF spectra.

Besides evidence for linear N$_3$ observed after dissociative ionization, there are additional features clearly visible in the m/z=28(N$_3^+$) and m/z=14(N$^+$) TOF spectra in Figs. 6 and 7. To simulate the observed spectra, several pathways had to be included. Information about some of these channels is already in hand. For example, if the linear-N$_3$ fragment dissociates in the ionizer due to electron impact, it is safe to assume that the less stable HEF-N$_3$ will dissociate as well. To include those secondary fragmentation processes, the translational energy distributions which are shown in Fig. 5 and the anisotropy parameters for both the fast and slow N$_3$ channels were used as input parameters without any additional modifications. In Figs. 6 and 7 their contribution to the signal is shown using red and green lines for the fragmentation of the fast N$_3$ and slow N$_3$, respectively.

**Unimolecular dissociation of HEF-N$_3$**

While this analysis assumes the fragmentation pattern of linear and HEF-N$_3$ to be similar, no amount of adjustment of the relative contributions of the slow and fast radical chan-
nels can reproduce the \( m/z = 28 \) and \( m/z = 14 \) data. In particular, the fastest appearing signal is far too translationally excited to be accounted for by either of these reactions. There is also signal in these TOF spectra that appears somewhat slower than would be expected. In the \( m/z = 28(N_3^+) \) TOF data, some of this is due to the molecular channel (blue), but this cannot explain the TOF quantitatively.

As pointed out earlier, the comparison of the observed \( m/z = 35(Cl^+) \) and the \( m/z = 42(N_3^+) \) TOF spectra and the corresponding translational energy distributions suggests that HEF-N_3 fragments with \( E_{\text{int}} \geq 11 \pm 2 \) kcal/mol (above the ground state of the HEF-N_3 isomer) undergo unimolecular dissociation, for example,

\[
N_3^+ \rightarrow N_2(X^1\Sigma_g^+) + N(^4S). \tag{8}
\]

For \( N_3 \) molecules with enough internal energy, reaction (8) can provide a substantial translational energy release. The contribution from this channel is shown (cyan) in Figs. 6 and 7.

Photodissociating \( \text{CIN}_3 \) at \( \lambda = 248 \) nm (hv = 115 kcal/mol) may form \( N_3 \) with enough internal energies to dissociate by the spin-allowed reaction,

\[
N_3^+ \rightarrow N_2(X^1\Sigma_g^+) + N(^4D). \tag{9}
\]

Product flux through this channel releases much less translational energy, as a great deal of the available energy is converted to \( N \)-atom electronic excitation. The contribution of this channel to the \( m/z = 28(N_3^+) \) and the \( m/z = 14(N^+) \) TOF spectra can be seen as magenta lines in Figs. 6 and 7, respectively.

To simulate these secondary processes, the translational energy distribution of the \( N_3 \) molecules dissociating through reaction (8) was found by taking the difference between the two \( P(E_T) \)'s shown in Fig. 5. This calculated translational energy distribution is used to model the laboratory flux of \( N_3 \) molecules that go on to dissociate. The previously described forward-convolution program\textsuperscript{35} then uses a “secondary” \( P(E_T) \) characterizing the translational energy release of reaction (8) to calculate the laboratory flux and the TOF spectra for \( N_3 \) and \( N_2 \). The secondary \( P(E_T) \) was iteratively adjusted to obtain the best fit. The same strategy was used to account for the \( N_3 \) molecules that undergo reaction (9). However, here the translation energy distribution of the dissociating \( N_3 \) molecules was assumed to be the product of the \( P(E_T) \) distribution for the \( \text{Cl} \) atom and a heavy-side step function at \( E_T = 12 \) kcal/mol, scaled to best fit the data.

**Photodissociation of \( N_3 \)**

Including the unimolecular dissociation of HEF-N_3 is clearly necessary to fit the \( m/z = 14 \) and 28 data. However, as can be seen in Fig. 6, especially in the inset in Fig. 6(b), none of the channels mentioned so far accounts for the fastest \( N_3 \) fragments. The fastest fragments can only be formed by a two-photon process, i.e., by secondary photodissociation of primary \( N_3 \) fragments. Consequently, an additional channel was included in the analysis simulating the photodissociation of \( N_3 \) fragments:

\[
N_3 + h\nu \rightarrow N_2(X^1\Sigma_g^+) + N(^4D). \tag{10}
\]

A thorough analysis, summarized in Figs. 8 and 9, was undertaken which attempted to model the data using photodissociation of either HEF- or linear \( N_3 \). Figure 8 shows the \( m/z = 28 \) and \( m/z = 14 \) TOF spectra for \( \Theta = 30^\circ \). The first row shows the best fits obtained to the data if one neglects secondary photodissociation of \( N_3 \) altogether. Although it is possible to fit the \( N^+ \) data, due the presence of the fast moving \( N \) atoms from NCI photodissociation, it is clear that the fastest \( N_3 \) fragments are not accounted for in this model.

This fast signal can be fitted assuming secondary photodissociation of \( N_3 \), as shown in the second row of spectra in Fig. 8. The data were fitted equally well using either of the two secondary \( P(E_T) \) distributions in Fig. 9 and an anisotropy parameter \( \beta = 0.7 \). The slower distribution in Fig. 8 assumes that the primary products are fast \( \text{Cl} + N_3 \), i.e., linear \( N_3 \) is dissociated by a second photon, while the faster distribution assumes the primary products to be slow \( \text{Cl} + N_3 \), with HEF-N_3 undergoing secondary dissociation. The fits to the data alone cannot distinguish these two possibilities. However, the vertical arrows in Fig. 9 show the maximum \( E_T \) values, \( E_T^{\text{max}} \), thermodynamically allowed from secondary photodissociation of linear and HEF-N_3, using the average value of the fast and slow Cl fragments (30 and 9 kcal/mol, respectively) to specify the \( N_3 \) internal energy. We find that \( E_T^{\text{max}} \) for HEF-N_3 matches the maximum in the secondary \( P(E_T) \) distribution assuming photodissociation of HEF-N_3, whereas \( E_T^{\text{max}} \) for linear \( N_3 \) lies considerably beyond the maximum of the corresponding secondary \( P(E_T) \) distribution. Figure 9 thus offers indirect evidence that most of the secondary photodissociation signal is from HEF-N_3.

**Overall fits to the \( N_3^+ \) and \( N^+ \) data**

In addition to the already described processes (dissociative ionization, unimolecular dissociation, and secondary photodissociation of \( N_3 \) photofragments) the primary molecular channel (1) had to be included in a complete analysis of the \( m/z = 28(N_3^+) \) TOF spectra. Because of the branching ratios of 95%/5% in favor of the radical channel, the contribution of the molecular channel forming \( N_3 \) and NCI is limited.\textsuperscript{4} The primary translational energy distribution shown in Fig. 3 was used without any changes and the respective contribution is shown as blue line in Fig. 6 and it is clearly visible that all six individual contributions add up nicely to fit the observed data.

The secondary photodissociation of NCI photoproducts was observed in the \( m/z = 35 \) TOF spectra and therefore reaction (7) had to be included in the analysis of the \( m/z = 14(N^+) \) data. NCI photodissociation was modeled using the secondary \( P(E_T) \) used to simulate the \( m/z = 35 \) data and an anisotropy parameter \( \beta = 1.1 \), indicating a parallel transition. The contributions from all described channels to the overall observed \( m/z = 14 \) signal are shown in Fig. 7.

**DISCUSSION**

The results presented above show that the fast and slow Cl fragments are correlated to the formation of linear \( N_3 \) and
HEF-N$_3$, respectively. The observed excitation energy of HEF-N$_3$ $\Delta E = 30.1 \pm 3$ kcal/mol agrees well with a previously determined excitation energy $31 \pm 2$ kcal/mol obtained from velocity maps of the Cl fragments at a somewhat different photolysis wavelength ($\lambda = 235$ nm). We now have two experiments with different product detection methods at two different wavelengths that both lead to a quantitatively indistinguishable heat of formation for the HEF-N$_3$. This adds further weight to the interpretation of the bimodal energy distribution as two isomers as opposed to a bimodal vibrational energy distribution of linear N$_3$. These experimental determinations are consistent with theoretical predictions of the heat of formation of the cyclic-N$_3$ isomer. Bitererova et al. calculated the excitation energy of cyclic N$_3$ to be 30.0 kcal/mol, in excellent agreement with these results and with results from Zhang et al. who calculated an energy difference of 30.3 kcal/mol. Although other explanations of the observed bimodal translational energy distributions still cannot be ruled out, this simple energy consideration shows that all experiments carried out so far on ClN$_3$ photodissociation under collision-free conditions are consistent with photolytic formation of cyclic N$_3$.

However, the data also indicate that N$_3$ isomers with internal energies of $E_{\text{int}} \gtrsim 11 \pm 2$ kcal/mol (with respect to the cyclic-N$_3$ minimum) undergo rapid unimolecular dissociation and therefore cannot be detected by our present experi-

FIG. 8. (Color) Time-of-flight spectra taken at $\Theta = 30^\circ$ for $m/z = 28(N_2^+)$ (left column) and $m/z = 14(N^+)$ (right column). The first row shows the best fits excluding any secondary photodissociation processes of N$_3$ fragments. The second and third rows show the best fit including photodissociation of linear and HEF-N$_3$ isomers, respectively. Each contribution is shown in the same color as in Figs. 6 and 7.
mental setup. Recently, Babikov et al. published a comprehensive study of the unimolecular dissociation of the N3 radical on the ground doublet and excited quartet potential-energy surfaces based on multireference single and double excitation configuration interaction and second-order multireference perturbation methods. The calculations, which do not include the influence of the geometric phase effect, suggest that the doublet-quartet surface crossings that lead to dissociation lie between 17 and 30 kcal/mol above the cyclic-N3 minimum.19 In Fig. 1 the observed threshold for dissociation (gray bar) is compared with the calculated thresholds and doublet-quartet seam crossings. Present theory does not allow us to understand the apparent dissociation threshold at 11 kcal/mol. Further theoretical work incorporating the geometric phase effect’s influence into doublet-quartet seam crossings may be necessary to resolve this discrepancy. It should be pointed out that some HEF-N3 is detected even when containing internal energies that exceed the doublet-quartet seam crossing calculated by theory.

The fact that the secondary dissociation products, N and N2, were detected and the corresponding TOF spectra could be analyzed successfully taking into account the unimolecular dissociation and secondary photodissociation of HEF-N3 provides further support for the photochemical mechanism derived from this work. The possibility that the observed slow CI channel arises from unimolecular dissociation of excited NCl fragments can be ruled out for several reasons. In a previous letter, it was shown that N2+NCI is a minor channel (5±3%) compared to the radical-forming N3+Cl channel (95±3%).4 Even if we would assume that N2+NCI is the main product and that it is because of the unimolecular dissociation of excited NCl primary photoproducts that not all of the NCI is detected, we still would miss the N2 and N counterfragments in the m/z =28 and m/z =14 TOF spectra. The dominant peak in the m/z =28(N2+) data appears at the same time as the strongest peak in the m/z =42(N3+) and the m/z =14(N+) data. The only reasonable explanation is dissociative ionization of the linear-N3 fragment in the ionizing region of the mass spectrometer. Therefore we confirm the previous analysis of N2 +NCI being a minor channel and that slow Cl fragments are actually formed by reaction (2a) and (2b).

CONCLUSIONS

We performed photofragment translational spectroscopy experiments to reveal the primary and secondary decomposition pathways of chlorine azide, ClN3, when photolyzed at λ=248 nm. Special attention is paid to the radical channel (2a) and (2b) forming Cl+N3 and the following secondary unimolecular dissociation and photodissociation processes of highly excited N3 fragments.

Bimodal translational energy distributions for both the Cl and the N3 fragments clearly show that two distinct forms of the N3 radical are produced. Besides the formation of the ground-state (linear azide) N3 radical a high-energy form (HEF) of N3 (possible cyclic N3) is formed.

The observed energy difference between the linear N3 and the HEF-N3 isomer of ΔE=30.1±3 kcal/mol agrees well with calculations performed by Bittererova et al.23 and previous velocity map imaging experiments at a different photolysis wavelength.1

Both forms of N3 were detected by electron-impact ionization. A lower limit of the lifetime of the HEF-N3 was determined to be τ≥100 μs.

N3 fragments with more than 11±2 kcal/mol of internal energy above the cyclic-N3 minimum appear to undergo unimolecular decomposition or photodissociation. The secondary N2 and N unimolecular dissociation fragments were detected and the observed translational energy distributions of those products were successfully interpreted by a chemical model where highly excited N3 radicals fragment into both N3(X 1Σ−)+N(5S) and N3(X 1Σ−)+N(5D). The fastest observed N and N2 fragments are produced by secondary photodissociation processes of the primary NCl and N3 photoproducts. There is indirect evidence that HEF-N3 is selectively photodissociated at 248 nm in the presence of linear azide.

The observed translational energy releases of both the N and N2 fragments cannot be explained by unimolecular decomposition of energized NCI fragments. Therefore, we rule this secondary process out as a source of the observed slow Cl fragments.

In summary, the velocity map imaging and the photofragment translational spectroscopy experiment carried out so far on this molecule are consistent with photolytic formation of cyclic N3—although the structure of the HEF-N3 species remains unclear and more work is needed.

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