Two photoionization thresholds of N₃ produced by ClN₃ photodissociation at 248 nm: Further evidence for cyclic N₃

Peter C. Samartzis
Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California 93106

Jim Jr-Min Lin, Tao-Tsung Ching, Chanchal Chaudhuri, and Yuan T. Lee
Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan, Republic of China

Shih-Huang Lee
National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Science-Based Industrial Park, Hsinchu 30077, Taiwan, Republic of China

Alec M. Wodtke
Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California 93106

(Received 6 June 2005; accepted 13 June 2005; published online 5 August 2005)

We present results of near-threshold photoionization of N₃ photofragments produced by laser photodissociation of ClN₃ at 248 nm. The time of flight of recoiling N₃ is used to resolve two photochemical channels producing N₃, which exhibit different translational energy release. The two forms of N₃ resolved in this way exhibit different photoionization thresholds, consistent with their assignment to linear (X ²Π₁) and cyclic N₃. This result agrees with the existing theoretical calculations of excited and ionic states of N₃ and strengthens previous experimental results which suggested that the ClN₃ photolysis produces a cyclic form of N₃. © 2005 American Institute of Physics. [DOI: 10.1063/1.1993590]

There has been substantial interest in the photochemistry of ClN₃ (Ref. 1) due to its importance in chemical lasers, yet only recently have we begun to understand its primary photochemical reactivity dynamics. ClN₃ photodissociation proceeds by two distinct pathways. The first (“molecular”) pathway produces NC1 and N₂ and the second (“radical”) pathway produces C1 and N₃. Photofragmentation translational spectroscopy (PTS) studies show that the radical channel is dominant (95%±3%) over the molecular channel at one of the more commonly used photolysis wavelengths (248 nm). Using velocity map ion imaging (VMI) of C1 atoms to study the dominant radical channel, Hansen and Wodtke concluded that N₃ is produced with a bimodal internal energy distribution when ClN₃ is photolysed at 235 nm, a behavior that was also later reported from PTS studies at 248 nm. Recently, more accurate thermochemical data along with high-level quantum-chemical computations helped to show that these observations are quantitatively consistent with the formation of N₃ in two isomeric forms: the ²Π₁ “linear” and the ²B₁/²A₂ “cyclic N₃.”

Theory predicts the cyclic-N₃ electronic ground state to have three equivalent energy minima of ²B₁ symmetry separated by low-energy (0.0386 eV) transition states of ²A₂ symmetry occurring pseudorotation. At the ²B₁ minima, cyclic N₃ has the shape of an acute isosceles triangle with one short (double—1.235 Å) bond and two long (single—1.467 Å) bonds while at the ²A₂ transition states it becomes an obtuse isosceles triangle with one long (1.5338 Å) and two short (1.3058 Å) bonds. The cyclic-N₃ isomer is predicted to lie 1.35 eV above linear azide and be frustrated by a large (1.5 eV) barrier to linearization. Furthermore the barrier to spin-forbidden dissociation forming N(²D)+N₂ is predicted to be larger than 1.4 eV. Quantum-chemical analysis of the doublet-quartet seam crossing reveals that cyclic N₃ is long lived with respect to dissociation to ground state products, N(²S)+N₂ (Ref. 7), a prediction consistent with a recent report of bimodal translational energy distributions for N₃ observed by PTS. Calculations show that the geometric phase effect is large in cyclic N₃.

Ab initio calculations on N₃ predict an equilateral triangular structure for the a’-¹A₁ state with a N–N bond length of 1.3314 Å. Its energy was calculated to be 0.871 eV above the N₃(¹Π₃) ground state. These authors refer to peaks in the photoelectron spectra of N₃ indicating states of N₃ that are 0.72 and 0.79 eV above the N₃ ground state to support their conclusions. Exploiting the literature value of the ionization energy of N₃(¹Π₃), 11.06 eV, one predicts that the a’-¹A₁ state should lie 11.931 eV above the linear-azide or 10.58 eV above the cyclic-N₃ state. Recent ab initio calculations carried out at CCSD(T)/cc-pVTZ level of theory predict the cyclic N₃ adiabatic ionization energy to be T calves = 10.39 eV (Ref. 13) (neglecting zero-point energy, ZPE). The ZPE (0.1644 eV) of the ground E-symmetry vibrational state of cyclic N₃ has been calculated carefully, including the geometric phase effect. The ZPE of cyclic N₃ (0.2421 eV) was calculated within the harmonic approximation. From
this, we arrive at a theoretically predicted ionization threshold, $T_{\text{00}} = 10.47$ eV. It is reasonable to assume that if the high-energy form of N$_3$ produced by ClN$_3$ photodissociation at 248 nm possesses a cyclic structure, its ionization will lead to the $\alpha^1 \rightarrow \beta_3$ state of N$_3^+$. If this is true, we expect to find the photoionization threshold for the excited form of N$_3$ close to the values predicted by theory.

The experiments discussed here were carried out at the Chemical Dynamics endstation of the 21A Beamline of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. We used synchrotron radiation to vary the photon energy used to ionize and detect N$_3$ fragments produced by ClN$_3$ laser photodissociation at 248 nm. By virtue of their differing translational energy releases, we are able to resolve the two forms of N$_3$ formed in the photodissociation and separately measure the photoionization thresholds for each. These results reveal a photoionization threshold for the energetic form of N$_3$ that is shifted to lower energy, consistent with the theoretically predicted energies described above. This provides additional evidence supporting the photochemical formation of cyclic N$_3$.

A description of the apparatus has been previously published and only a brief description of the experiment will be given here. A mix of ClN$_3$ seeded in He carrier gas was prepared by passing a 10% Cl$_2$ mix in He over moist NaN$_3$ suspended in a cotton wool and then through a drying agent (Drierite) to remove excess water. The mix expanded supersonically through a solenoid valve (General Valve, Series 9) in the source chamber of the apparatus forming a molecular beam which was intersected at right angles, 54 mm downstream by the cylindrically focused output (2.25 $\times$ 8.5 mm$^2$ spot size) of a KrF excimer laser (Lambda Physik LPX 210) operating at 248 nm. The photodissociation fragments were allowed to drift for another 100.5 mm through two separate differentially pumped chambers and were then intersected at right angles by synchrotron radiation (1.0 $\times$ 1.0 mm$^2$ spot size) in a cryogenically cooled ultrahigh-vacuum ionization chamber.

The beamline radiation characteristics are available online. In these experiments, the photon energy spread of the fundamental synchrotron radiation in the 9.8–13-eV range is ~3% full width at half maximum (FWHM). Higher-order harmonics produced by the synchrotron undulator were filtered by appropriate noble gasses. The photoions were focused by ion optics into a quadruple mass filter and the $m/z$ ratio of choice was detected by a Daly-type detector and counted by a multichannel scaler. The molecular beam is rotatable, allowing the measurement of time-of-flight (TOF) spectra at different laboratory angles $\Theta$ between the molecular beam and the detection axis. Initially we recorded the TOF spectra of $m/z = 35$ (Cl$^+$) at a 13.3 eV synchrotron energy and of $m/z = 42$ (N$_3^+$) in the 9.8–13 eV synchrotron energy range in 0.3 eV steps at $\Theta = 20^\circ$, 40$^\circ$, and 60$^\circ$. Measurements for $m/z = 42$ were repeated for $\Theta = 20^\circ$, 45$^\circ$, 50$^\circ$, and 80$^\circ$ in steps as small as 0.04 eV in the 10.2–11.5 eV range to obtain a more accurate value for the ionization thresholds. Each TOF spectrum was averaged for $5\times10^4$ laser shots as needed to have adequate signal-to-noise ratio.

TOF spectra obtained in this fashion were fitted by the PHOTRON forward-convolution program. This program simulates the time-of-flight spectrum based on center-of-mass coordinates.

![Image](https://example.com/image.png)

**FIG. 1.** Representative TOF spectra of ClN$_3$ → Cl$^+$ + N$_3$ photolysis at 248 nm. Fast and slow channels have been previously attributed to formation of electronic-ground-state linear azide and a high-energy form of N$_3$ consistent with “cyclic” N$_3$, respectively. As the high-energy form of N$_3$ appears with lower translational energy release than that of linear azide, the two channels can be resolved in these TOF spectra. The momentum-matched Cl photofragment must and does exhibit a similar bimodal character. The Cl$^+$ TOF spectra shown here employed 13.3 eV photons for the photoionization of Cl. The N$_3^+$ TOF spectra shown here employed 10.7-eV photons for photoionization. Experimental data are represented as filled circles, slow and fast N$_3$ channel fits as dotted and dashed lines, respectively, and the total fit as continuous line. The Y axis shows ion counts per laser shot, normalized to the laser power.
translational energy distributions $P(E)$ which are iteratively adjusted until a satisfactory fit to the data is obtained. Beam velocity, laboratory angle, dissociation and ionization intersection sizes, finite angular acceptance angle of the detector, laser power, and polarization are additional program parameters.

Representative fitted TOF spectra for $m/z=35$ (Cl$^+$) and $m/z=42$ (N$_3^+$) are presented in Fig. 1 for two laboratory angles $\Theta$. All TOF distributions are bimodal, exhibiting a “fast” and a “slow” component. The fast Cl$^+$ peak corresponds to production of ground linear azide; the slow peak corresponds to formation of the high-energy form of N$_3$, consistent with cyclic N$_3$. The ratio of the integrated areas of the two components is about 4:1, consistent with previous experimental measurements. For $m/z=42$ (N$_3^+$), the slow peak is also clearly visible, however, the ratio between the fast and slow components changes with photoionization wavelength, indicating that the two forms of N$_3$ have different photoionization properties.

Fitting data like that of Fig. 1 allows us to determine the relative contributions of the fast and slow channels at many photoionization wavelengths. The integrated intensity of each channel is shown as a function of ionizing photon energy in Fig. 2 for laboratory angles of $\Theta=45^\circ$ (top panel) and $20^\circ$ (bottom panel). In each plot, the filled circle points belong to the fast channel and the open rectangles to the slow channel. Intensities were normalized to the maximum of the respective channel at 11.5-eV synchrotron energy.

Both channels exhibit an abrupt increase in intensity between 10.2 and 11.2 eV. For the fast channel, the observed threshold agrees well with the previously determined photoionization threshold for linear N$_3$ at 11.06 eV, indicated in Fig. 2 by the solid arrows. The slow channel clearly exhibits a lower photoionization threshold, around 10.6 eV, which is close to the theoretically derived value for ionization of cyclic N$_3$ producing $a^1A_1 N_3^+$ (indicated in Fig. 2 by the dashed arrows).

We note that at all laboratory angles, ion signal is present well below the respective ionization threshold energies. Synchrotron radiation produced from an undulator exhibits higher harmonics. Thus, light that is nominally of a photon energy of 10.2 eV has other photon energies present (20.4 eV, 40.8 eV, etc.). The inset in the upper panel shows the 45° data on an expanded scale. A Gaussian function centered at 10.62 eV represents the energy spread of the synchrotron radiation. The solid arrows indicate the literature value for the ionization threshold of linear N$_3$ and the dashed arrows the expected value for cyclic N$_3$. Statistical error bars were calculated at 90% confidence for the 45° data points where more than two measurements were available using the student’s t-test. The error bars shown for 20° are estimated based on comparison with the 45° data.

FIG. 2. Photoionization of the two TOF-resolved forms of N$_3$ vs ionization photon energy. Normalized integrated intensities for the slow (open rectangles) and fast (filled circles) channels at laboratory angles of $\Theta=20^\circ$ (lower panel) and $45^\circ$ (upper panel). The inset in the upper panel shows the 45° data on an expanded scale. A Gaussian function centered at 10.62 eV represents the energy spread of the synchrotron radiation. The solid arrows indicate the literature value for the ionization threshold of linear N$_3$ and the dashed arrows the expected value for cyclic N$_3$. Statistical error bars were calculated at 90% confidence for the 45° data points where more than two measurements were available using the student’s t-test. The error bars shown for 20° are estimated based on comparison with the 45° data.
eV, 40.8 eV, ...). Nearly all of this light is removed by the
gas filter; however, the filtering is not effective for photons in
the transparent window of the gas. This effect increases the
background in the measurement but does not change the dif-
fERENCE in the ionization thresholds for the two forms of N₃.

In conclusion, we observe two photoionization threshold
energies for the two forms of N₃ that are formed in ClN₃
photolysis at 248 nm. The observed thresholds are consistent
with assignments of the two forms of N₃ to (1) electronic
ground-state linear azide and (2) cyclic N₃. This result sug-
gests that the ionization of cyclic N₃ leads to the a'−1A₁ ion
state.

ACKNOWLEDGMENTS

This work was in part supported by a grant from the Air
Force Office of Scientific Research (Grant No. FA9550-04-
1-0057. One of the authors (P.C.S.) would like to thank the
Institute of Atomic and Molecular Sciences, Academia
Sinica, Taipei, Taiwan for financial support and the National
Synchrotron Radiation Research Center personnel for their
help in conducting those experiments.

75, 2177 (1981); R. D. Coombe, J. V. Gilbert, S. S. Beaton, and N.
Mateljevic, J. Phys. Chem. A 106, 8422 (2002); A. V. Komissarov, G. C.
3 A. M. Wodtke, N. Hansen, J. C. Robinson, N. E. Sveum, S. J. Goncher,
Phys. Lett. 368, 568 (2003); N. Hansen, A. M. Wodtke, A. V. Komissa-
(2003).
(2005).
122, 044315 (2005).
10 N. Hansen, A. M. Wodtke, S. J. Goncher, J. Robinson, N. Sveum, and D.
47, 1231 (1982).
13 V. Mozhayskiy and A. I. Krylov (private communication).
15 http://srrcbl.nsrrc.org.tw/servlet/blDocReader?param=21A