# Dissociative photoionization of $ClN_3$ using high-resolution synchrotron radiation: The N–Cl bond energy in $ClN_3$

Alfredo Quinto-Hernandez [d],*, Yin-Yu Lee [a], Tzu-Ping Huang [a], Wan-Chen Pan [a], Jim Jr-Min Lin [b], Petia Bobadova-Parvanova [c], Keiji Morokuma [c], Petros C. Samartzis [d], Alec M. Wodtke [d]

[a] *National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 30077, Taiwan, ROC*
[b] *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan, ROC*
[c] *Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322, United States*
[d] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106-9510, United States*

## Abstract

High-resolution synchrotron-radiation-based photoionization mass spectrometry was applied to study the dissociative photoionization of $ClN_3$ under collision-free molecular beam conditions at ionization energies between 10 and 17 eV. No parent ion ($ClN_3^+$) could be detected under our experimental conditions. This suggests that the ground and excited states of $ClN_3^+$ are weakly bound or repulsive, a conclusion supported by electronic structure calculations also reported here. We recorded photoionization yield spectra at $m/z = 49, 42, 35$ and 14 from which we extracted the appearance potentials for $NCl^+$, $N_3^+$, $Cl^+$, and $N^+$. The appearance potential of $NCl^+$ ($10.17 \pm 0.02$ eV) observed here is close to the previously reported ionization potential of $ClN_3$ obtained form photoelectron spectroscopy. Using the theoretically calculated binding energy of $ClN_3^+$ (0.2 eV), we derive an estimate of the *adiabatic* ionization potential of $ClN_3 = 9.97 \pm 0.02$ eV. The measured appearance potentials for $N_3^+$, $Cl^+$, and $N^+$ provide three independent determinations of the Cl–N bond energy in $ClN_3$, which agree within their respective error limits. The observations of this work are consistent with a new value of the N–Cl bond energy in $ClN_3$, $D_0(Cl–N_3) = 1.86 \pm 0.05$ eV, 0.3 eV lower than previously reported values, which are however experimentally derived upper limits. The bond energy reported here is consistent with high level *ab initio* (CCSD(T)) electronic structure calculations extrapolated to the complete basis set limit, which yield a value: $D_0(Cl–N_3) = 1.87$ eV.

## 1. Introduction

Interest in $ClN_3$ and its photochemistry has increased in the last few years, sparked by the identification of $NCl(a^1\Delta)$ as an energy carrier in a chemical iodine laser [1–6] as well as by the discovery of a radical dissociation pathway thought to produce – among other photoproducts – a cyclic isomer of $N_3$ [7–10]. This activity has also prompted a series of new theoretical calculations on $N_3$ neutral and cation [11–15]. Thanks to this recent flurry of work, we now know that UV photolysis of $ClN_3$ proceeds through two primary dissociation pathways:

$$ClN_3 \rightarrow NCl + N_2 \qquad (1)$$

$$ClN_3 \rightarrow Cl + N_3 \qquad (2)$$

where accurate measurements have been possible, reaction (2) is found to be the dominant dissociation pathway [8,16].

In contrast, still little is known about the ionization of $ClN_3$. The only experimental measurement of the $ClN_3$ ionization potential, 10.2 eV, comes from Frost et al. who used photoelectron spectroscopy [17]. Hansen et al. used velocity map imaging to look at $ClN_3$ multi-photon ionization at 202 nm and in the absence of detectable $ClN_3^+$ they determined that the parent ion, if stable, should have a dissociation barrier less than 0.28 eV [18]. The results suggest that the ionization potential reported by Frost et al. does not lead to the $ClN_3^+$ parention.

In this work, we have carried out a systematic investigation of the dissociative photoionization of $ClN_3$. Specifically, we have used high-resolution, tunable synchrotron radiation and the collision-free conditions of a molecular beam to measure

---

* Corresponding author. Tel.: +1 805 893 5035; fax: +1 805 893 4120.
*E-mail address:* aquinto@chem.ucsb.edu (A. Quinto-Hernandez).

photoionization yield spectra of $NCl^+$, $N_3^+$, $Cl^+$ and $N^+$ ions resulting from $ClN_3$ dissociative ionization in the 10–17 eV range. Our data confirm that $ClN_3^+$ is unstable in this energy range, dissociating through four channels, each appearing at different a photon energy. We identify these appearance potentials with good precision, from which we are able to re-evaluate the lowest dissociation energy of $ClN_3$.

## 2. Experimental

The measurements reported here were performed on the 21B U9-CGM beamline of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Detailed descriptions of the apparatus have been reported previously [19,20], and only a brief explanation of the experiments will be given here. A mixture of $ClN_3$ in He was prepared by passing a 10% mixture of $Cl_2$ in He first over moist sodium azide ($NaN_3$) suspended in cotton wool to produce $ClN_3$ and then through a drying agent (Drierite) to remove any excess water. The $ClN_3$ mix expanded supersonically through a pulsed valve (General valve or Even-Lavie valve) to form a molecular beam which, after passing a collimating skimmer, was photoionized by tunable, high-resolution, VUV synchrotron radiation. The generated ions were then mass-selected by a quadrupole mass filter and the mass-to-charge ratio ($m/z$) of choice was detected by a channeltron detector. By tuning the synchrotron radiation wavelength, we were able to record photoionization spectra for $m/z = 42$ ($N_3^+$), 35 ($Cl^+$), 49 ($NCl^+$) and 14 ($N^+$), produced by dissociative ionization of $ClN_3$ in 10–17 eV ionization energy range. Despite intense efforts, we were unable to observe $m/z = 77$ or 79 ($ClN_3^+$) in the 10–17 eV range. Attempts to observe $N_2^+$ (from the $N_2^+ + NCl$) were foiled by a ubiquitous $N_2$ background.

High-resolution synchrotron radiation was produced by passing the undulator output (bandwidth-FWHM ∼3%) through a monochromator resulting in tunable VUV radiation with a bandwidth of 0.15 meV (FWHM) tunable in steps as small as ∼0.02 meV. Higher undulator harmonics were suppressed by noble gas (Xe or Ar) in a gas cell positioned after the monochromator, similar to the design presented by Suits et al. [21]. Using the same gas cell as an absorption cell and measuring the synchrotron radiation emerging from the cell, we measured several absorption lines of Xe and Ar which were used for precise wavelength calibration of the monochromator.

The *ab initio* electronic structure theory calculations were carried out using conventional coupled cluster CCSD(T) (coupled cluster single and doubles with perturbative triples) treatment of electronic correlation [22] and the cc-pVxZ families of basis sets [23–26] with increasing levels of sophistication ($x = 3(T)$, 4(Q), and 5). The geometries of $ClN_3$ and $N_3$ were optimized and harmonic frequencies (from which zero point energies were derived) were calculated by numerical differentiation of the analytic gradient at the CCSD(T)/cc-pVTZ level of theory. Improved energy values for larger basis sets were obtained as single-point calculations at this optimized geometry. All calculations were performed using the Gaussian 03 program package [27].
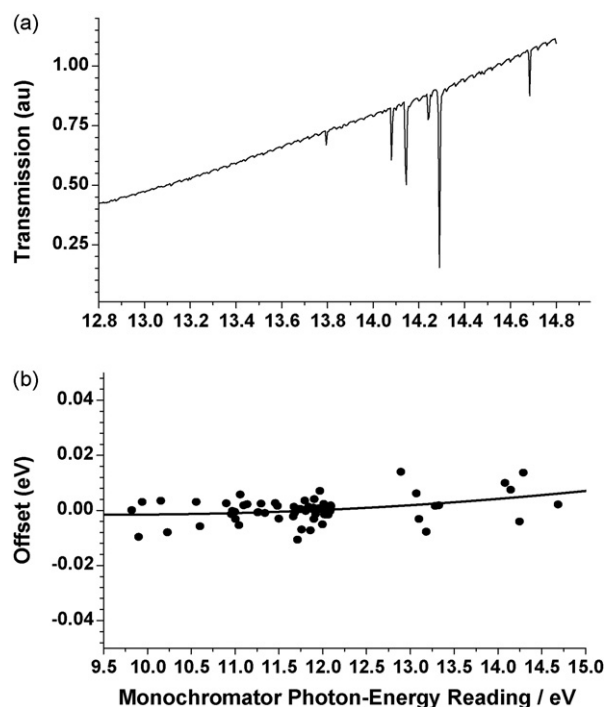


Fig. 1. Energy calibration. (a) An example Ar absorption spectrum. (b) The deviation (marked as ●) of apparent vs. observed Xe and Ar absorption lines is shown as a function of energy and is fit with a polynomial function. The polynomial equation obtained is $Y = 0.02508 - 0.00558X + 2.9232 \times 10^{-4}X^2$ and its coefficients suggest that differences do not change significantly with ionization energy in this range, with the maximum deviation being around ±0.02 eV.

The complete basis set limit (CBS) was evaluated performing focal point analysis [28] of the cc-pVxZ data. The Hartree–Fock energies were extrapolated using $x = 3$, 4, and 5 and the exponential form of Feller et al. [29,30]. The correlation energies were extrapolated using $x = 4$ and 5 and the integrated Schwartz expression [31].

## 3. Results and discussion

The results section is organized as follows. First, we present the energy calibration resulting from the analysis of Xe and Ar absorption spectra. Second, we evaluate the lowest ionization threshold of $ClN_3$ and comment on the low stability of the parent ion, $ClN_3^+$, including an estimate of the adiabatic ionization potential of $ClN_3$. Third, we present three dissociative ionization potential (Ion appearance potentials) and evaluate the $D_0(Cl–N_3)$ from each.

### 3.1. Energy calibration

To test the calibration of the monochromator over our energy range, we recorded absorption spectra of Xe (in 9.8–12.1 eV) and Ar (12–14.8 eV) (e.g., Fig. 1a) and compared with known transition energies [32] (Fig. 1b). Only the strongest lines observed were used for the calibration. In Fig. 1b, we matched the apparent absorption energies with literature values [32] and computed the deviation (observed-actual). It is evident from Fig. 1b that even apparent energy measurements are within 0.02 eV of the
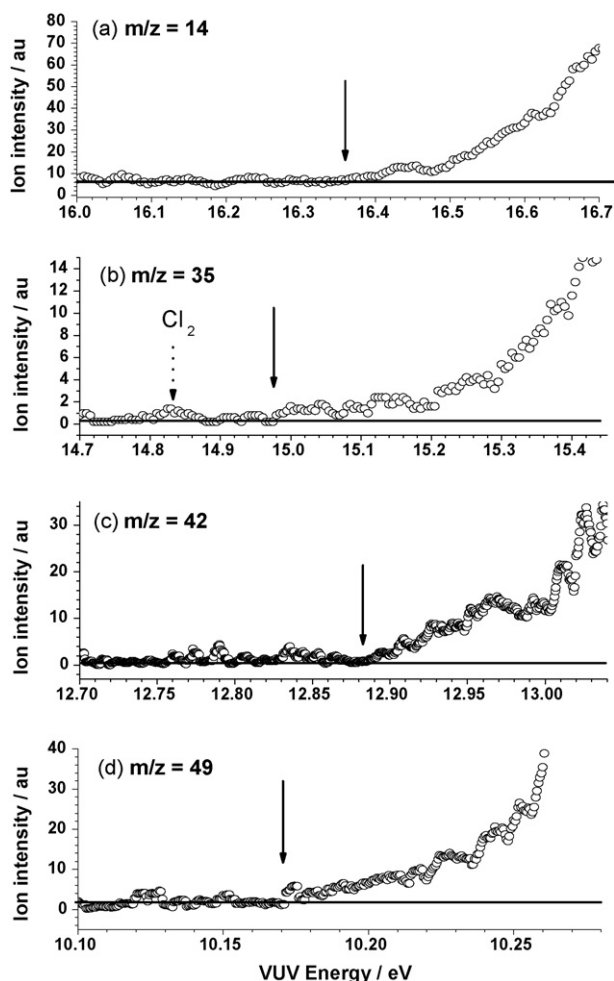
Fig. 2. Photoionization spectra near threshold for: (a) $m/z = 14$ ($N^+$), (b) 35 ($Cl^+$), (c) 42 ($N_3^+$) and (d) 49 ($NCl^+$), produced by reactions on Table 1. The experimentally measured spectra are shown as open circles and a solid line shows the average background signal in each spectrum present well below threshold. Data are shown re-binned as described in text. The detected ion signal indicated by a dashed arrow in the range 14.8–14.88 eV corresponds to the dissociation of molecular chlorine: $Cl_2^+ \rightarrow Cl^+ + Cl$.

Table 1
Appearance thresholds (in eV) for $ClN_3$ dissociative photoionization

| Reaction | Threshold (eV) |
|---|---|
| $ClN_3(X^1A') + h\nu_{sync} \rightarrow NCl^+ + N_2 + e^-$ | $10.17 \pm 0.02$ |
| $ClN_3(X^1A') + h\nu_{sync} \rightarrow N_3^+ + Cl + e^-$ | $12.88 \pm 0.06$ |
| $ClN_3(X^1A') + h\nu_{sync} \rightarrow Cl^+ + N_3 + e^-$ | $14.98 \pm 0.05$ |
| $ClN_3(X^1A') + h\nu_{sync} \rightarrow N^+ + N_2 + Cl + e^-$ | $16.36 \pm 0.06$ |

these spectra, we determined the appearance threshold for each ion as the energy at which the ion signal rises detectibly above the background signal. To guide the eye, we have drawn lines along the average background signal seen well below threshold. Working in this fashion we obtained four appearance potentials (Table 1) all of which are dissociative. From lowest energy to highest, these thresholds correspond to formation of $NCl^+ + N_2$, $N_3^+ + Cl$, $Cl^+ + N_3$ and $N^+ + Cl + N_2$.

A pitfall of this kind of work should be noted. Sometimes in the past, ion-pair thresholds have been mis-assigned as appearance potentials [33–35]. While it is reasonable to question if the appearance potentials reported here might suffer from similar problems, we are re-assured by the large magnitudes of the electron affinities of Cl (3.614 eV) and $N_3$ (2.68 eV). Although we did not specifically look for negative ions during this work, these large electron affinities mean that the observed appearance potentials are much higher than the ion pair thresholds, making them easy to distinguish.

As mentioned above, we were unsuccessful in finding any experimental conditions where a stable $ClN_3^+$ ion could be identified. These results strongly suggest that the previously reported $ClN_3$ ionization potential obtained from photoelectron spectroscopy [17] ($10.2 \pm 0.01$ eV) results from *dissociative* ionization producing $N_2 + NCl^+$, as argued by Hansen et al. [18]. MP2/aug-cc-pVTZ and CCSD[T]/cc-pVTZ calculations (structures from which are shown in Fig. 3) support this conclusion. Electronic structure calculations on the most stable structure of $ClN_3^+$ show an ion-quadrupole complex ($NCl^+ \ast N_2$) with a binding energy of only 0.39 eV at MP2 and 0.20 eV at CCSD(T) level. Due to the large change in geometry from the parent neutral $ClN_3$, we can easily understand why near threshold, ionization leads to a vibrationally excited $ClN_3^+$ with more than enough energy to dissociate. From the MP2 calculations and the experimentally derived $AP_{NCl+}$ value, we may estimate the adiabatic ionization potential of $ClN_3$ to be $9.97 \pm 0.02$ eV.

### 3.3. The dissociation energy of $ClN_3$ derived from three dissociative appearance potentials

Conservation of energy dictates that the appearance energies measured for $N_3^+ + Cl$ and $Cl^+ + N_3$ in this experiment should equal the sum of the dissociation energy of $ClN_3$ plus the ionization energy of the respective ion plus a possible barrier for the specific channel. For the $N_3^+ + Cl$ channel this statement can be written down mathematically as follows:

$$AP_{N_3^+} = D_0(Cl-N_3) + IP(N_3) + B_2 \tag{3}$$

true value. As will become apparent below, the uncertainty in the determination of the ionization thresholds is larger than 0.02 eV, due to signal-to-noise limitations. Therefore, one might consider obtaining thresholds without any energy calibration at all. Nevertheless, we fitted the data of Fig. 1 to a polynomial and used this function to correct the energy readout of the monochromator. The energy corrections are less than 10 meV.

### 3.2. $ClN_3$ ionization threshold and $ClN_3^+$ stability

In Fig. 2a–d, we show mass resolved photoionization yield spectra for $m/z = 14$ ($N^+$), 35 ($Cl^+$), 42 ($N_3^+$), and 49 ($NCl^+$). The original data, taken at 0.005 eV steps for $N^+$, $Cl^+$ and $NCl^+$ and 0.0005 eV for $N_3^+$, has been re-binned (i.e., adjacent point averaging, such that each open circle corresponds to 0.0150 eV for $m/z = 14$ and $m/z = 35$, 0.0076 eV for $m/z = 42$, and 0.0040 eV for $m/z = 49$). This procedure provides the optimal signal-to-noise ratio, which is important to the threshold determinations. From
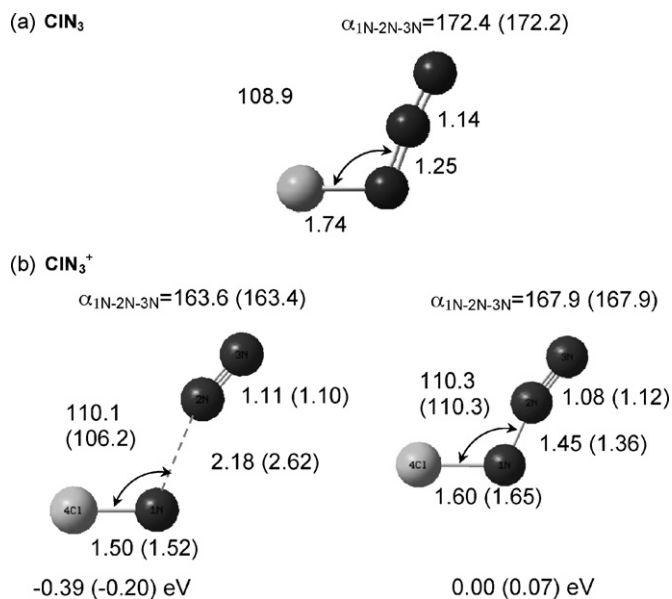
Fig. 3. Geometries of $ClN_3$ and $ClN_3^+$ calculated at MP2/aug-cc-pVTZ and CCSD[T]/cc-pVTZ levels. (a) The structure of $ClN_3$ neutral; (b) Two energy minima of $ClN_3^+$. The figure on the right side corresponds to the geometry which is close to $ClN_3$, and on the left to the lower-energy van der Waals complex ($NCl^+ \ast N_2$, ion-quadrupole). Bond lengths are given in Å, angles in degrees. The CCSD(T) results are shown in parentheses.

Table 2
CCSD(T) calculations of $Cl$–$N_3$ bond energies using different basis sets with increasing level of sophistication

| Basis set | $D_0(Cl$–$N_3)$ | ZPE | $D_0(Cl$–$N_3)$ |
|---|---|---|---|
| cc-pVTZ | 1.72 | −0.07 | 1.65 |
| cc-pVQZ | 1.84 | −0.07[a] | 1.77 |
| cc-pV5Z | 1.89 | −0.07[a] | 1.82 |
| CBS limit | 1.94 | −0.07[a] | 1.87 |

Data are corrected for zero-point vibrational energy (ZPE). The complete basis set limit (CBS) is evaluated after focal point analysis of the cc-pVxZ data (see text). All energies are in eV.

[a] The cc-pVTZ value is used.

where $B_2$ signifies the barrier of the channel leading from $ClN_3^+$ to $N_3^+ + Cl$.

Using the measured $AP_{N_3^+} = 12.88$ eV and the literature value for $D_0(Cl$–$N_3) = 2.15 \pm 0.1$ eV [7] and IP (linear $N_3$) $= 11.06 \pm 0.01$ eV [36], one obtains a value of $B_2 = -0.33$ eV, a negative barrier, which is unphysical. There are two ways one might reconcile this outcome results. First, the existence of vibrationally excited $ClN_3$ in the molecular beam would lead to hot bands and reduced appearance potentials. Second, the previously determined upper limit to $D_0(Cl$–$N_3) = 2.15$ eV might be too high. First, we consider hot bands. The $Cl$–$N_3$ stretch at $545$ cm$^{-1}$, the out-of-plane bend at $522$ cm$^{-1}$ and even the in-plane bend at $719$ cm$^{-1}$ [18,37] can be significantly populated (3–7%) before molecular beam expansion. Furthermore, these vibrations are of high enough frequency that they may not be relaxed completely in the molecular beam. On the other hand, one quantum of any of these modes is insufficient to explain the apparent 0.33 eV discrepancy indicated above. Indeed, three to four quanta would be needed, which appears to us highly unlikely. Furthermore, such a contribution from hot bands to ion signal should be observed in other photoionization channels and not only in the threshold determination of $N_3$ presented above; however, no evidence of hot bands can be found in those data.

In light of this discussion, the most plausible explanation of our results appears to suggest a revision of the $D_0(Cl$–$N_3)$. Assuming a value of $B_2 \equiv 0$ eV, we obtain from Eq. (3), a value of $D_0(Cl$–$N_3) = 1.82 \pm 0.05$ eV. This value is also, in principle, an upper limit to the dissociation energy of $ClN_3$ as $B_2$ is not necessarily zero. Note that production of ro-vibrationally excited $N_3^+$ would further reduce the derived bond energy.

One should note that this new value is not inconsistent with previous experimental work on $ClN_3$ [7–9,16]. However, both velocity map imaging (VMI) and photofragment translational spectroscopy (PTS) results rely on the assumption that the fragments with the maximum observed kinetic energy have little or no internal energy. Therefore, those determinations of $D_0(Cl$–$N_3)$ are in error to the extent that the fastest observed $N_3$ fragments possess internal energy. Comparing the deductions from this work to those obtained by VMI, we suggest that an additional 0.33 eV was channeled into ro-vibrational excitation of the linear $N_3$ photofragments even for the fastest observed fragments. Given the bent geometry of the $Cl$–$N$–$N$ bonding in $ClN_3$, its dissociation could trigger substantial rotational and bending vibration excitation in $N_3$ fragment.

One previous theoretical study found $D_0(Cl$–$N_3) = 2.1051$ eV at the MP2 level [38]. It would appear that higher levels of theory are required to get more accurate results. Consequently, we performed a series of high-level CCSD(T) calculations using the cc-pVxZ families of basis sets with increasing levels of sophistication ($x = 3$(T), $4$(Q), and 5). This allowed us to evaluate the complete basis set limit (CBS) by performing focal point analysis of the cc-pVxZ data. The results are shown in Table 2. As can be seen, our highest level estimate CCSD(T)/CBS + ZPE(CCSD(T)/cc-pVTZ) gives a $D_0(Cl$–$N_3)$ value of 1.87 eV, consistent with this lower experimental value.

The appearance potential analysis for the $Cl^+ + N_3$ channel can be made considering Eq. (4), which is analogous to Eq. (3)

$$AP_{Cl^+} = D_0(Cl - N_3) + IP(Cl) + B_3 \qquad (4)$$

Applying Eq. (4) to the appearance energy for $Cl^+ + N_3$ channel (14.98 eV), $D_0(Cl$–$N_3) = 1.86$ eV and $IP(Cl^+) = 12.96$ eV [39] we obtain a barrier $B_3 = 0.17_{(+0.1, -0.2)}$ for this channel. Alternatively, we might assume that the $B_3 \equiv 0$, where we would derive an independent value of $D_0(Cl$–$N_3) = 2.03_{(+0.1, -0.2)}$. Here, the error bars are large and asymmetrical due to the very gradual rise in signal at threshold. See Fig. 2b.

We can follow a similar procedure to determine the barrier $B_4$ for the $N^+$ appearance channel:

$$B_4 = AP_{N^+} - D_0(Cl - N_3) - D_0(N - N_2) - IP(N)$$
$$= 16.36 - 1.86 - (-0.05) - 14.53 = 0.02 \text{ eV}$$

Here, we have used the literature value $D_0(N$–$N_2) = -0.05$ eV obtained from accurate translational energy release measurements on $N_3 \rightarrow N_2 + N$ photodissociation [40,41].
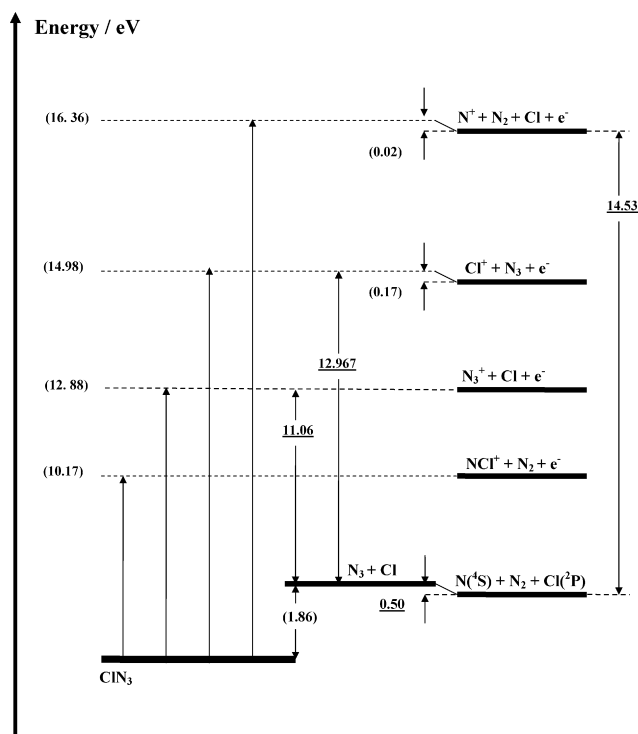
Fig. 4. Energy diagram for the processes discussed in the text employing the results derived from this work (shown in parentheses). The appearance potentials obtained in this work are designated by solid arrows. Barriers $B_1$–$B_4$ are all zero within the inherent uncertainty of the experiments. Literature values are underlined.

Alternatively we may assume $B_4 \equiv 0$ and use the experimentally determined $AP_{N^+} = 16.36$ eV to obtain an independent measure of $D_0(Cl–N_3) = 1.88 \pm 0.05$ eV. The energetics summarized in Table 1 are also shown in Fig. 4.

In summary we obtain three independent measures of the N–Cl bond energy in $ClN_3$ from three dissociative ionization thresholds: $D_0(Cl–N_3) = [1.82 \pm 0.05$ eV, $2.02_{(+0.1, -0.2)}$, $1.88 \pm 0.05$ eV], which all agree within experimental error limits. We calculate an average, weighted by the inverse squared-error, and recommend the value $D_0(Cl–N_3) = 1.86 \pm 0.05$ eV. This is about 0.3 eV lower than previous accepted values. One should realize that due to the nature of the experiments, even this lower value constitutes an upper limit, depending on the height of the dissociative ionization barrier in each channel and the degree of ro-vibrational excitation of the measured ions (and that of unmeasured neutrals).

## 4. Conclusions

We report for the first time mass-resolved photoionization yield spectra of $NCl^+$, $N_3^+$, $Cl^+$ and $N^+$ ions from molecular beam cooled $ClN_3$. Ionization of $ClN_3$ proceeds through at least four dissociative channels leading to different products at different dissociation energies. The previously reported ionization potential of $ClN_3$ is shown to correspond to the appearance potential of $NCl^+$. Theoretical calculations of the ground state of this ion, show it to be only weakly bound (0.2 eV at the CCSD(T) level) and best described as an ion quadrupole com-

plex. We derive an estimate of the adiabatic ionization potential of $ClN_3$ (9.97 eV). We also measured the appearance potentials for $Cl^+$, $N_3^+$ and $N^+$, providing three independent means of deriving the Cl–N bond energy in $ClN_3$, $D_0(Cl–N_3)$. These results are in agreement with one another, from which we recommend a revision of this bond energy to the following: $D_0(Cl–N_3) = 1.86 \pm 0.05$ eV, about 0.3 eV less than presently accepted values. High level *ab initio* electronic structure calculations in the complete basis set limit are in excellent agreement with this value.

## References

[1] A.J. Ray, R.D. Coombe, J. Phys. Chem. 99 (1995) 7849.
[2] T.L. Henshaw, G.C. Manke, T.J. Madden, M.R. Berman, G.D. Hager, Chem. Phys. Lett. 325 (2000) 537.
[3] A.T. Pritt, R.D. Coombe, Int. J. Chem. Kinet. 12 (1980) 741.
[4] R.D. Coombe, S.J. David, T.L. Henshaw, D.J. May, Chem. Phys. Lett. 120 (1985) 433.
[5] R.D. Coombe, J. Opt. Soc. Am. A-Opt. Image Sci. Vision 3 (1986) 70.
[6] N. Hansen, A.M. Wodtke, A.V. Komissarov, M.C. Heaven, Chem. Phys. Lett. 368 (2003) 568.
[7] N. Hansen, A.M. Wodtke, J. Phys. Chem. A 107 (2003) 10608.
[8] N. Hansen, A.M. Wodtke, S.J. Goncher, J.C. Robinson, N.E. Sveum, D.M. Neumark, J. Chem. Phys. 123 (2005) 104305.
[9] P.C. Samartzis, N. Hansen, A.M. Wodtke, Phys. Chem. Chem. Phys 8 (2006) 2958.
[10] P.C. Samartzis, J.J.M. Lin, T.T. Ching, C. Chaudhuri, Y.T. Lee, S.H. Lee, A.M. Wodtke, J. Chem. Phys. 123 (2005) 051101.
[11] D. Babikov, B.K. Kendrick, P. Zhang, K. Morokuma, J. Chem. Phys. 122 (2005) 044315.
[12] D. Babikov, P. Zhang, K. Morokuma, J. Chem. Phys. 121 (2004) 6743.
[13] D. Babikov, V.A. Mozhayskiy, A.I. Krylov, J. Chem. Phys. 125 (2006) 084306.
[14] P. Zhang, K. Morokuma, A.M. Wodtke, J. Chem. Phys. 122 (2005) 014106.
[15] V.A. Mozhayskiy, D. Babikov, A.I. Krylov, J. Chem. Phys. 124 (2006) 224309.
[16] A.M. Wodtke, N. Hansen, J.C. Robinson, N.E. Sveum, S.J. Goncher, D.M. Neumark, Chem. Phys. Lett. 391 (2004) 334.
[17] D.C. Frost, C.B. Macdonald, C.A. Mcdowell, N.P.C. Westwood, Chem. Phys. 47 (1980) 111.
[18] N. Hansen, A.M. Wodtke, A.V. Komissarov, K. Morokuma, M.C. Heaven, J. Chem. Phys. 118 (2003) 10485.
[19] Y.Y. Lee, T.Y. Dung, J.Y. Yu, Y.F. Song, K.T. Hsu, K.K. Lin, J. Electron Spectrosc. Relat. Phenom. 144 (2005) 29.
[20] Y.F. Song, J.Y. Yuh, Y.Y. Lee, S.C. Chung, L.R. Huang, K.D. Tsuei, S.Y. Perng, T.F. Lin, H.S. Fung, C.I. Ma, C.T. Chen, K.L. Tsang, Rev. Sci. Instrum. 77 (2006) 085102.
[21] A.G. Suits, P. Heimann, X.M. Yang, M. Evans, C.W. Hsu, K.T. Lu, Y.T. Lee, A.H. Kung, Rev. Sci. Instrum. 66 (1995) 4841.

[22] J.A. Pople, M. Headgordon, K. Raghavachari, J. Chem. Phys. 87 (1987) 5968.
[23] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.
[24] R.A. Kendall, T.H. Dunning, R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
[25] D.E. Woon, T.H. Dunning, J. Chem. Phys. 103 (1995) 4572.
[26] A.K. Wilson, T. vanMourik, T.H. Dunning, J. Molec. Struct. Theochem. 388 (1996) 339.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T.K. Vreven, N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, Y.H.T. Nakajima, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03 Revision C.02 (2004).
[28] J.P. Kenny, W.D. Allen, H.F. Schaefer, J. Chem. Phys. 118 (2003) 7353.
[29] D. Feller, J. Chem. Phys. 96 (1992) 6104.
[30] D. Feller, J. Chem. Phys. 98 (1993) 7059.
[31] T. Helgaker, W. Klopper, H. Koch, J. Noga, J. Chem. Phys. 106 (1997) 9639.
[32] A.E. Kramida, W.C. Martin, A. Musgrove, E.B. Saloman, C.J. Sansonetti, J. Reader, J.J.C. Curry, NIST Atomic Spectra Database Version 3.1.0, http://physics.nist.gov/PhysRefData/ASD/index.html.
[33] G.K. Jarvis, K.M. Weitzel, M. Malow, T. Baer, Y. Song, C.Y. Ng, Phys. Chem. Chem. Phys 1 (1999) 5259.
[34] A.M. Wodtke, Y.T. Lee, J. Phys. Chem. 89 (1985) 4744.
[35] Y. Ono, C.Y. Ng, J. Chem. Phys. 74 (1981) 6985.
[36] J.M. Dyke, N.B.H. Jonathan, A.E. Lewis, A. Morris, Mol. Phys. 47 (1982) 1231.
[37] A. Schulz, I.C. Tornieporthoetting, T.M. Klapotke, Inorg. Chem. 34 (1995) 4343.
[38] M. Otto, S.D. Lotz, G. Frenking, Inorg. Chem. 31 (1992) 3647.
[39] R.D. Lide, CRC Handbook of Physics and Chemistry, CRC Press, Boca Raton, FL, 1992.
[40] R.E. Continetti, D.R. Cyr, D.L. Osborn, D.J. Leahy, D.M. Neumark, J. Chem. Phys. 99 (1993) 2616.
[41] R.E. Continetti, D.R. Cyr, R.B. Metz, D.M. Neumark, Chem. Phys. Lett. 182 (1991) 406.