Dissociative Photoionization of ClN_3 Using High-Resolution Synchrotron Radiation: The N–Cl Bond Energy in ClN_3

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High-resolution 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 by using synchrotron radiation at NSRRC 21B/U9-CGM beamline. No parent ion (ClN_3+) could be detected under our experimental conditions. This suggests that the ground and excited states of ClN3+ are weakly bound or repulsive, a conclusion supported by electronic structure calculations using conventional coupled cluster CCSD(T)/cc-pVxz treatment. We recorded photo-ionization yield spectra at m/z= 49, 42, 35 and 14 from which we extracted the appearance potentials for NCl^+, N_3^+, Cl^+, and N^+.

Appearance thresholds (in eV) for ClN3 dissociative photoionization

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

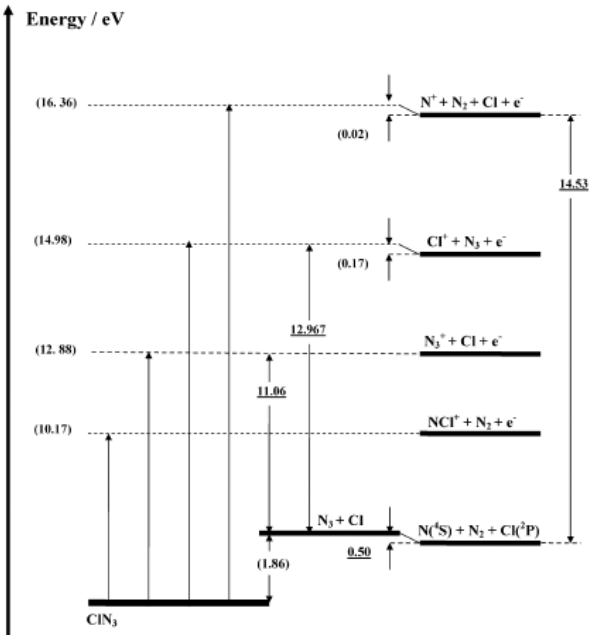

Figure 1. Energy diagram for the processes discussed employing the results derived from thiswork (shown in parentheses). The appearance potentials obtained in this work are designated by solid arrows.

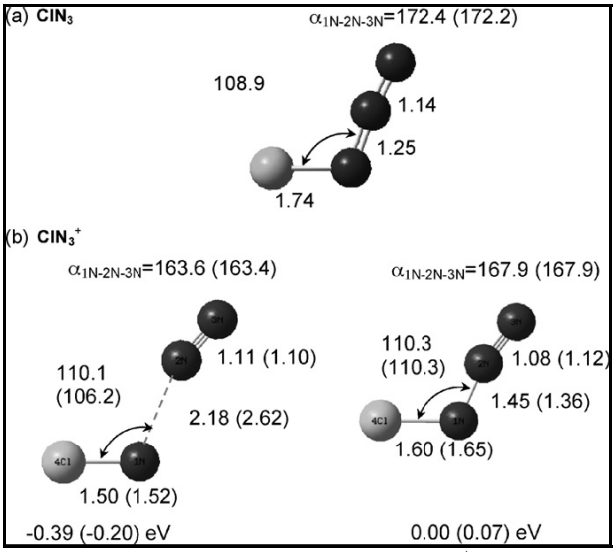

Figure 2. Geometries of ClN_3 and ClN_3^+ calculated at MP2/aug-cc-pVTZ and CCSD[T]/cc-pVTZ levels. (a) The structure of ClN_3 neutral; (b) Two energy minima of ClN_3^+. The figure on the right side corresponds to the geometry which is close to ClN_3, and on the left to the lower-energy van derWaals complex (NCl^+*N_2, ion-quadrupole). Bond lengths are given in Å, angles in degrees. The CCSD(T) results are shown in parentheses.

The appearance potential of NCl^+ (10.17±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±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, from the zero point energy level D_0 (Cl–N_3) = 1.86±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.