PHOTOIONIZATION AND FRAGMENTATION DYNAMICS OF ClN_3

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The photoionization and fragmentation dynamics of ClN_3 have been examined using 203 nm excitation with (2+1) REMPI detection of the N_2 product. Kinetic energy and angular distributions of N_2 and NCl^+ were characterized by velocity map imaging. The N_2 product was formed with appreciable rotational excitation, with population in levels as high as J=90. Velocity map images for the J=50 fragment showed that the maximum energy released to translation was 1.14 eV. This result indicated that the N_2 did not come from the expected channel, $ClN_3 + h\nu \longrightarrow NCl(a^1\Delta) + N_2$, which would produce much more energetic fragments. Velocity maps of N_2 and NCl^+ were consistent with the process

$$ClN_3 + 2h\nu \longrightarrow NCl^+ + N_2$$

The observed kinetic energy distributions of the N_2 and NCl^+ photoproducts are consistent with the formation of vibrationally excited NCl^+. The velocity maps of photoelectrons peaked near zero velocity, showing that ClN_3^+ is formed with nearly all excess energy in vibration. *Ab initio* calculations (CCSD(T)/cc-pVTZ) confirm that ClN_3^+ is unstable with respect to decomposition to NCl^+ and N_2. In combination, the experimental and theoretical results can be used to obtain the thermodynamics of the $ClN_3 + h\nu \longrightarrow NCl(a^1\Delta) + N_2$ reaction. The fact that products correlating with NCl(a) could not be observed suggests that the state of ClN_3 accessed by 203 nm excitation does not undergo direct dissociation.