

ELECTRONIC SPECTROSCOPY OF THE JET-COOLED HPCI FREE RADICAL

BRANDON S. TACKETT, SHENG-GUI HE, COREY J. EVANS, and DENNIS J. CLOUTHIER, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*; RICHARD H. JUDGE, *Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141-2000*.

The $\tilde{A}^2A' - \tilde{X}^2A''$ electronic transition of the HPCI free radical has been observed by laser-induced fluorescence (LIF) spectroscopy in the 458 - 400 nm region. HPCI and DPCI were generated in a pulsed discharge jet using a precursor mixture of PCl_3 and H_2 or D_2 in argon. At low resolution the bands have the characteristic rotational contour of a perpendicular transition of an asymmetric top, with additional axis switching branches due to the low symmetry of the molecule. At high resolution, small K_a dependent spin splittings are found which confirm that the molecule contains a single unpaired electron. Our studies of the LIF and wavelength resolved emission spectra have established most of the vibrational frequencies of HPCI and DPCI and the molecular structures in the ground and excited states have been obtained from rotational analyses of the 0_0^0 bands of both isotopomers. The analysis of the spectra, rotational constants, vibrational frequencies, molecular geometries and the results of CCSD(T) *ab initio* calculations of the molecular parameters will be discussed.