ELECTRONIC SPECTROSCOPY OF THE JET-COOLED HPCl FREE RADICAL

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The $\tilde{\mathrm{A}}\ ^2A'$ - $\tilde{\mathrm{X}}\ ^2A''$ electronic transition of the HPCl free radical has been observed by laser-induced fluorescence (LIF) spectroscopy in the 458 - 400 nm region. HPCl and DPCl 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 HPCl and DPCl 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.