ELECTRONIC SPECTROSCOPY OF JET-COOLED HCP^+

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Laser-induced fluorescence spectra of jet-cooled HCP^+ and DCP^+ have been obtained with the pulsed discharge technique using HCP/DCP and argon precursor mixtures. Most of the excited state vibrational fundamentals have been observed and a set of vibrational constants obtained. High resolution spectra of the $^2\Pi_{3/2}$ components of the 0_0^0 bands of both isotopomers have been recorded, and these spectra show resolved phosphorus hyperfine structure which allowed the determination of the excited state Fermi contact parameter. The B values were used to obtain the ground and excited state effective geometric parameters as r_0''(CH) = 1.077(2) Å, r_0''(CP) = 1.6013(3) Å, r_0'(CH) = 1.082(2) Åand r_0'(CP) = 1.5331(3) Å. The ground state vibrational energy levels reported in the literature were fitted to a Renner-Teller hamiltonian that included the effects of angular momentum coupling as well as spin-orbit, vibrational anharmonicity and Fermi resonance effects.