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 ${}^{0}_{0}$ 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) Å and 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.