PHOSPHORUS HYPERFINE STRUCTURE IN THE ELECTRONIC SPECTRUM OF THE HPCl FREE RADICAL

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The 444 nm 2_0^1 bands of the $\tilde{A}^2A'$ - $\tilde{X}^2A''$ transition of the jet-cooled $HP^{35}Cl$ and $HP^{37}Cl$ radicals have been studied at high resolution using the pulsed electric discharge technique with a precursor mixture of PCl_3 and H_2. Spectra recorded with linewidths of 360 MHz revealed resolved hyperfine structure in both isotopomers arising from the excited state Fermi contact interaction of the unpaired electron with the magnetic moment of the ^{31}P nucleus, with a'_F = 0.0641(10) cm^{-1} and 0.0636(31) cm^{-1} for $HP^{35}Cl$ and $HP^{37}Cl$, respectively. No contribution from the ground state, or excited state contributions from the hydrogen or chlorine nuclei were resolved, confirming *ab initio* predictions that HPCl is a $p\pi$ radical in the $\tilde{X}$ state, and an $s\sigma$ radical with a substantial contribution from the phosphorus $3s$ atomic orbital in the $\tilde{A}$ state. The free atom comparison method has been used to estimate that the singly occupied molecular orbital in the excited state has 14% phosphorus $3s$ character.