INVESTIGATING STRUCTURE AND BONDING IN FREE RADICALS: MEASURING HYPERFINE STRUCTURE IN EXCITED ELECTRONIC STATES

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The $A^3\Pi$ - $X^3\Sigma^-$ electronic band system of the PH radical has been investigated at high resolution with a novel narrow bandwidth injection seeded optical parametric oscillator based on β-barium borate crystals. The OPO is pumped by the third harmonic from a single mode Nd:YAG laser and is seeded by an external cavity diode laser in the near infrared. This provides high power pulsed light simultaneously in the near infrared (idler) and the visible (signal) spectral regions at a resolution of $\sim$100 MHz. The tuneable ultraviolet light required to probe the A - X electronic transition of the PH radical is generated by sum frequency mixing the signal wave with the second harmonic from the pump laser. The overall sub-Doppler resolution obtained in the ultraviolet allows hyperfine splittings due to the different possible orientations of the nuclear spin to be observed. Since the experimentally determinable hyperfine parameters contain expectation values over the co-ordinates of the valence electrons with unquenched spin or orbital angular momentum, they provide a direct route to unravelling the composition of the molecular wavefunction. Analysis of the observed hyperfine structure in the $A^3\Pi$ state of PH is presented in terms of the electronic structure of the molecule.