LASER SPECTROSCOPY AND DYNAMICS OF THE JET-COOLED AsH_2 FREE RADICAL

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The $\tilde{A}^2A_1$ - $\tilde{X}^2B_1$ electronic transition of the jet-cooled AsH_2 free radical has been studied by laser-induced fluorescence (LIF), wavelength-resolved emission, and fluorescence lifetime measurements. The radical was produced by a pulsed electric discharge through a mixture of arsine (AsH_3) and high-pressure argon at the exit of a pulsed valve. Nine vibronic bands were identified by LIF spectroscopy in the 505-400 nm region, including a long progression in the bending mode and two bands (1_0^1 and $1_0^12_0^1$) involving the excited state As-H symmetric stretch. Single vibronic level emission spectra showed similar activity in the bending and symmetric stretching frequencies of the ground state. High- resolution spectra of the 0_0^0 band exhibited large spin-splittings and small, resolved arsenic hyperfine splittings, due to a substantial Fermi contact interaction in the excited state. The rotational constants obtained in the analysis gave effective molecular structures of r_0'' = 1.5183(1) Å, θ_0'' = 90.75(1)^o and r_0' = 1.4830(1) Å, θ_0' = 123.10(2)^o. The excited state fluorescence lifetimes vary dramatically with rovibronic state, from a single value of 1.4 μs to many with lifetimes less than 10 ns, behavior which we interpret as signaling the onset of a predissociative process in the excited state.