DISCOVERY OF THE ELECTRONIC SPECTRA OF HPS AND DPS

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The hitherto unknown electronic spectrum of the closed shell transient molecule HPS has been observed in the 685 - 846 nm region by laser-induced fluorescence and single vibronic level emission techniques. HPS (and DPS) were produced in a pulsed electric discharge jet using a precursor mixture of 3% PH_3 and 1% H_2S (or PD_3 and D_2S) in high pressure argon. The weak set of observed bands are assigned to the $\tilde{A}^1\mathrm{A}'' - \tilde{X}^1\mathrm{A}'$ electronic transition on the basis of chemical evidence, isotope shifts and the correspondence of the vibrational frequencies, excitation energy, and band contours with predictions based on our own high level *ab initio* calculations. Theory predicts that the HPS bond angle decreases on electronic excitation, contrary to expectations based on Walsh diagrams.