

EXPERIMENTAL AND THEORETICAL STUDIES OF THE ELECTRONIC SPECTRA OF THE THIOPHOSPHORYL ($X_2P=S$) AND ARSENYL ($X_2As=O$) FREE RADICALS

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Small prototypical thiophosphoryl and arsenyl free radicals have been observed in the gas phase by laser-induced fluorescence (LIF) methods. The electron configuration of these species is similar to that of formaldehyde except there is an additional unpaired electron so the ground state is $...(\pi)^2 (n)^2 (\pi^*)^1 (^2A')$. The first electronic excited state ($^2A''$) generated by $n - \pi^*$ electronic excitation is calculated to occur in the infrared, so we assign the observed transitions as $\tilde{B}^2A' - \tilde{X}^2A'$ involving $\pi - \pi^*$ excitation. These assignments are confirmed by comparing the ground and excited state vibrational frequencies and excitation energies obtained from emission and LIF spectra to the results of our own *ab initio* calculations. The properties of the \tilde{B} excited state, which has the same symmetry as the electronic ground state, were calculated using the equations-of-motion coupled cluster singles and doubles methods available in the ACES II program package.