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

MOHAMMED A. GHARAIBEH, XIAOPENG ZAHNG, JIE WEI, YONG SHI, DENNIS J. CLOUTHIER, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*; SHENG-GUI HE, *Beijing National Laboratory for Molecular Science, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, The Chinese Academy of Sciences, Zhongguancun, Beijing,100080 People's Republic of China*.

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 - π^* electronic excitation is calculated to occur in the infrared, so we assign the observed transitions as $\tilde{B}^2A'$ - $\tilde{X}^2A'$ involving π - π^* 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.