AZOLE PHOTOELECTRON SPECTROSCOPY

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Ultraviolet Negative Ion Photoelectron Spectroscopy has been used to investigate the properties of the low-lying electronic states of the pyrrolyl, imidazolyl, and pyrazolyl radicals. The anions of these radicals were obtained from a hydroxide ion deprotonation of the respective parent azole in a flowing afterglow ion source. Subsequent collisions of the anions with the 0.5 Torr Helium buffer gas cooled them to room temperature. The ground state of the pyrrolyl radical has been assigned as $^2A_2$, with an adiabatic electron affinity of 2.145 ± 0.010 eV. Imidazolyl radical has been assigned a $^2B_1$ ground state and an adiabatic electron affinity of 2.613 ± 0.010 eV. Pyrazolyl radical, however, has nearly degenerate $^2A_2$ and $^2B_1$ states, and vibronic mixing plays a role in the appearance of the spectrum; we have assigned the ground state as $^2A_2$, with an adiabatic electron affinity of 2.939 ± 0.015 eV, and a term energy for the $^2B_1$ state of 0.031 ± 0.015 eV. Several vibrational bands were observed in each of the radical states, yielding gas phase vibrational frequencies. Additionally, using a thermodynamic cycle involving gas phase acidities and electron affinities, we have experimentally determined N-H bond dissociation energies for each parent molecule. This work is supported by the National Science Foundation and the Air Force Office of Scientific Research.