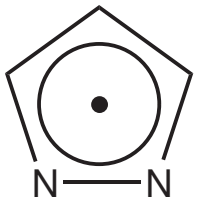
PHOTOELECTRON SPECTROSCOPY OF PYRAZOLIDE ANION: THREE LOW-LYING ELECTRONIC STATES OF THE PYRAZOLYL RADICAL

ADAM J. GIANOLA, TAKATOSHI ICHINO, and W. CARL LINEBERGER, *JILA and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309*; JOHN F. STANTON, *Institute for Theoretical Chemistry and Department of Chemistry and Biochemistry, University of Texas, Austin, TX 78712*.



The 351 nm photoelectron spectrum of pyrazolide anion has been measured. Pyrazolide is prepared by OH^- deprotonation of pyrazole in He buffer gas in a flowing-afterglow tube. Photodetachment from the anion leads to the formation of pyrazolyl radical in near-degenerate electronic states. The ground state is assigned as $^2A_2$, with an adiabatic electron affinity of 2.939 ± 0.010 eV, and a term energy for the lowest excited state ($^2B_1$) of 0.031 ± 0.001 eV. Franck-Condon simulation under the Born-Oppenheimer approximation fails to reproduce the spectrum, indicating strong vibronic coupling in the radical. Coupled cluster calculations have been carried out to evaluate the vibronic coupling constants at the geometry of the pyrazolide ground state. Strong interactions of the pseudo-Jahn-Teller type between the $\tilde{X}\ ^2A_2$ and $\tilde{A}\ ^2B_1$ states of pyrazolyl have been found for in-plane asymmetric modes that distort the five-membered ring, analogous to the $^2E''$ state of an isoelectronic Jahn-Teller system, cyclopentadienyl. While the $^2E''$ state in cyclopentadienyl is relatively well separated from the σ states, the same is not true in pyrazolyl; interactions with the nearby $\tilde{B}\ ^2B_2$ state result in further complication of the potential energy surface of the radical. Simulation of the observed spectrum has been attempted with the three-state coupling taken into account. A spectrum has also been measured for deuterated pyrazolide to help with the assignments of the vibronic bands. Supported by the National Science Foundation and the Air Force Office of Scientific Research.