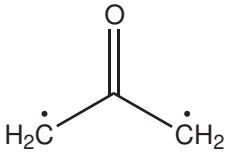
ELECTRONIC STRUCTURE OF OXYALLYL DIRADICAL: A PHOTOELECTRON SPECTROSCOPIC STUDY

TAKATOSHI ICHINO, REBECCA L. HOENIGMAN, ADAM J. GIANOLA, DJANGO H. ANDREWS, and W. CARL LINEBERGER, *JILA and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309*; WESTON T. BORDEN, *Department of Chemistry, University of North Texas, Denton, TX 76203*; STEPHEN J. BLANKSBY, *Department of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia*.



The 351 nm photoelectron spectrum of oxyallyl anion has been measured. The anion is synthesized via reaction of atomic oxygen anion with acetone in He buffer gas in a flowing-afterglow tube. Photodetachment leads to the formation of a "diradical" species, oxyallyl, which is isoelectronic with trimethylenemethane (TMM). Both CASSCF(4,4) and B3LYP/6-311++G(d,p) electronic structure calculations have been carried out for Franck-Condon simulation of the spectrum. The $^3B_2$ state of oxyallyl appears in the spectrum with a $400 \pm 40\ \mathrm{cm}^{-1}$ vibrational progression of the C-C-C bending motion. Angular distributions of the photoelectrons reveal that the $^1A_1$ state lies very close in energy to the $^3B_2$ state. We tentatively assign the $^1A_1$ state as the ground state, with an electron affinity of 1.945 ± 0.010 eV. The term energy for the $^3B_2$ state is 0.056 ± 0.005 eV. These observations contrast with the photoelectron spectrum of TMM anion. The effects of oxygen substitution on the electronic structure of the diradical are discussed. The photoelectron spectrum of cyclopentanone-2,5-diyl radical anion has also been obtained. The spectrum indicates that the electronic ground state of the diradical, cyclopentanone-2,5-diyl, is $^1A_1$, and the electron affinity is 1.659 ± 0.010 eV. The $^3B_2$ state of the diradical is also observed in the spectrum with a term energy of 0.243 ± 0.010 eV. The constraint on the geometric structure of the diradical due to the five-membered ring perturbs the singlet-triplet energy levels. Supported by the National Science foundation and the Air Force Office of Scientific Research