A NEGATIVE ION PHOTOELECTRON SPECTROSCOPIC AND COMPUTATIONAL STUDY OF Mo_2 AND Mo_2^-

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We report the 488 and 514 nm anion photoelectron spectra of Mo_2^-. Neutral Mo_2 has been described in recent $ab\ initio$ studies as having a bond order of six, predicted to be the highest of any homonuclear diatomic, exceeding even that of Cr_2(five). The photoelectron spectrum of Mo_2^- confirms the previously measured vibrational frequency of gas phase Mo_2 and displays transitions to vibrational levels up to v=7 in its $^1\Sigma_g^+$ ground state. The electron affinity of Mo_2 is measured to be 0.732 $\pm$ 0.010 eV. The Mo_2^- ground state is assigned as a $^2\Sigma_u^+$ state, in which the extra electron occupies a formally antibonding σ_u orbital of primarily $5s$ atomic parentage. A Franck-Condon analysis of the vibrational band intensities indicates a change in the equilibrium bond length of only 0.03 $\pm$ 0.02 Å upon electron detachment. These results, and the similar vibrational frequencies measured for Mo_2 and Mo_2^-, suggest that the anion HOMO is essentially nonbonding. Weak photodetachment transitions to excited states of Mo_2 lying within 1.2 eV of its ground state are also observed. DFT calculations using the BPW91/SDD method show good agreement with experiment for the electron affinity of Mo_2 and the bond lengths in the anion and neutral molecule ground states. It is hoped that these spectroscopic results will motivate and assist high level theoretical studies of the Mo_2^- anion.