A NEGATIVE ION PHOTOELECTRON SPECTROSCOPIC AND COMPUTATIONAL STUDY OF CrCu AND MoCu.

BEAU J. BARKER, STEPHEN R. MILLER, and DOREEN G. LEOPOLD, *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455*.

The early-late mixed metal dimers CrCu and MoCu and their anions were studied using negative ion photoelectron spectroscopy and density functional theory (DFT). The photoelectron spectra, obtained at 488 nm with an instrumental resolution of about 5 meV (40 cm^{-1}), provide measurements of electron affinities (0.912 +/- 0.005 eV CrCu, 1.010 +/- 0.010 eV MoCu), bond length changes upon electron detachment, vibrational frequencies and anharmonicities for the neutral congeners and their anions, and energies of their observed excited electronic states. Comparison of these data with the results of DFT B3LYP calculations indicate that both CrCu and MoCu have a $^6\Sigma^+$ ground state with a single σ bond of primarily 4*s* atomic parentage. In the anions, the extra electron singly occupies an antibonding σ^* orbital, giving a $^7\Sigma^+$ ground state. The electrons in the filled Cu $3d^{10}$ subshell appear to remain atom-localized and nonbonding. These conclusions conflict with the previous assignment[a] of a $^4\Sigma$, triply-bonded ground state for CrCu, based on the results of matrix ESR experiments.

[a] C. A. Baumann, R. J. Van Zee and W. Weltner, Jr. *J. Chem. Phys.* **79**, 5272 (1983).