A NEGATIVE ION PHOTOELECTRON SPECTROSCOPIC AND COMPUTATIONAL STUDY OF CrV AND MoV

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The heteronuclear diatomic metal ions CrV^- and MoV^- were investigated using negative ion photoelectron spectroscopy. These bare, heteronuclear group 5 and 6 transition metal dimers allow the study of multiple metal-metal bonding free of ligand effects. The photoelectron spectra, obtained at 488 nm with an instrumental resolution of about 5 meV (40 cm^{-1}), provide measurements of the electron affinities, vibrational frequencies for both the anion and neutral states, bond length changes upon electron detachment, excited electronic state energies and spin-orbit splittings. The CrV^- and MoV^- spectra display transitions to the multiply-bonded $^2\Delta$ $(d\pi)^4(d\delta)^3(d\sigma)^2(s\sigma)^2$ ground states of the neutral molecules and to several excited states. Addition of an electron to the vacant σ^* orbital gives the $^3\Delta$ anion, which is found to be the ground state of CrV^- but a low lying excited state of MoV^-. Addition of a dδ electron yields the $^1\Sigma^+$ MoV^- ground state. Density functional theory calculations of the anions and neutrals were performed to help elucidate the spectroscopic assignments and observed periodic trends.