Cluster cations of transition metals are produced in a laser vaporization source, and separated by mass in an initial linear time-of-flight (TOF) stage. The selected cluster is then fragmented by multiphoton dissociation with a YAG pumped dye laser. A reflectron TOF stage measures the mass and intensity of the resulting species. Photofragment intensity distributions, and multiphoton dissociation spectra of cooled niobium dimer cations and a measurement of the dissociation energy of zirconium dimer cations are presented. The lowest ground state of Nb$^{+2}$ was determined by all density functional calculations to be quartet-sigma. The electronic transition spectra of Nb$^{+2}$ implies that its dissociation energy, $D_e$, is equal to (or less than) 6.0 eV. The dissociation energy of the zirconium dimer cation has been accurately measured to be 4.20 $\pm$ 0.01 eV by multiphoton dissociation of the Zr$^{+2}$. The lowest ground state of zirconium dimer cation was determined to be doublet-sigma by two density functional calculations, but the other density functional calculations failed due to partially occupied molecular orbitals. The coefficients of the molecular wave function showed that it should be doublet-delta. The dissociation energy calculations of Nb$^{+2}$ and Zr$^{+2}$ were in agreement with their expermentical values within a few percentage error.