The copper complexes were prepared by laser-vaporization in a molecular beam and probed with threshold photoionization and pulsed field ionization-zero electron kinetic energy (ZEKE) spectroscopic methods. The ZEKE spectra showed the adiabatic ionization potentials of the Cu-E(CH₃)₃ (E = N, P, As) complexes in the order of P < As < N, although the difference between the phosphine and arsine complexes was much smaller than that from the amine species. Moreover, the spectra revealed intermolecular and ligand vibrations. For instance, the stretching frequencies were 269/199, 214/187, and 188/155 cm⁻¹ for the Cu⁺/Cu-N, Cu⁺/Cu-P, and Cu⁺/Cu-As, respectively.