Comprehensive thermochemistry for the hydration of copper ions

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Cross sections for the threshold collision-induced dissociation (TCID) of Cu\(^{2+}\)(H\(_2\)O)\(_n\), where \(n = 8 - 10\), and of CuOH\(^+\)(H\(_2\)O)\(_n\), where \(n = 1 - 4\), are measured using a guided ion beam tandem mass spectrometer. In both cases, the primary dissociation pathway is found to be loss of a single water molecule followed by the sequential loss of additional water molecules. In the Cu\(^{2+}\) complexes, charge separation to form CuOH\(^+\)(H\(_2\)O)\(_3\) and H\(^+\)(H\(_2\)O)\(_3\) is also observed and CuOH\(^+\)(H\(_2\)O) competitively loses both H\(_2\)O and OH. The data are analyzed using a statistical model after accounting for internal and kinetic energy distributions, multiple collisions, and kinetic shifts to obtain 0 K bond dissociation energies (BDEs). In addition, BDEs for the loss of OH from CuOH\(^+\)(H\(_2\)O)\(_n\) where \(n = 0 - 4\) are derived using the experimental BDEs for dissociation of CuOH\(^+\)(H\(_2\)O)\(_n\) and literature values for Cu\(^+\)(H\(_2\)O)\(_n\). Experimental BDEs are compared to theoretical BDEs determined at several levels of theory with reasonable agreement. Structural information regarding complexes of CuOH\(^+\)(H\(_2\)O)\(_n\), where \(n = 2 - 9\), are also obtained using infrared photodissociation spectroscopy (IRPD) in the OH stretching region and comparison to theoretical spectra. The IRPD spectra of all complexes where \(n \geq 3\) are consistent with structures generally having a coordination number (CN) of 4 although CuOH\(^+\)(H\(_2\)O)\(_7\) exhibits bands characteristic of both CN = 4 and CN = 5 isomers.