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Comprehensive thermochemistry for the hydration of copper ions

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Cross sections for the threshold collision-induced dissociation (TCID) of $\text{Cu}^{2+}(\text{H}_2\text{O})_n$, where $n = 8 - 10$, and of $\text{CuOH}^+(\text{H}_2\text{O})_n$, 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 $\text{CuOH}^+(\text{H}_2\text{O})_3$ and $\text{H}^+(\text{H}_2\text{O})_3$ is also observed and $\text{CuOH}^+(\text{H}_2\text{O})$ competitively loses both H_2O 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 $\text{CuOH}^+(\text{H}_2\text{O})_n$ where $n = 0 - 4$ are derived using the experimental BDEs for dissociation of $\text{CuOH}^+(\text{H}_2\text{O})_n$ and literature values for $\text{Cu}^+(\text{H}_2\text{O})_n$. Experimental BDEs are compared to theoretical BDEs determined at several levels of theory with reasonable agreement. Structural information regarding complexes of $\text{CuOH}^+(\text{H}_2\text{O})_n$, 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 $\text{CuOH}^+(\text{H}_2\text{O})_7$ exhibits bands characteristic of both $\text{CN} = 4$ and $\text{CN} = 5$ isomers.