INFRARED SPECTRA OF ANIONIC COINAGE METAL-WATER COMPLEXES

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We have studied the interaction of atomic coinage metal anions with water molecules by infrared photodissociation spectroscopy of $\mathrm{M}^- \cdot \mathrm{H_2O} \cdot \mathrm{Ar}_n$ clusters (M = Cu, Ag, Au; $n = 1, 2$). We discuss our observations in the framework of calculations on density-functional and coupled-cluster levels of theory. The gold anion is bound to the water molecule by a single ionic hydrogen bond, similar to the halide-water complexes. In contrast, zero-point motion in the silver and copper complexes leads to a deviation from this motif. The coinage metal anions thus introduce a new motif into the structures of hydrated anions for hydrated Cu^- and Ag^-. The concepts of single (SIHB) versus double (DIHB) ionic H bonds no longer hold for these systems. Although the equilibrium structures exhibit C_s symmetry SIHB motifs, the C_{2v} transition states are very low in energy. As a consequence, the ground-state wave functions explore very different geometries, permitting both OH groups to interact with the anion. The patterns of resulting infrared spectra are between those expected for SIHB and DIHB motifs, showing H bonding for both OH groups, but favoring asymmetric structures.