A theoretical study of uranyl solvation: explicit modelling of the second hydration sphere by quantum mechanical methods

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The inclusion of an explicit partial second sphere in the hydration of the uranyl ion is investigated by DFT-based quantum-mechanical methods. We design and study various complexes that are consistent with the established first-sphere coordination. These model complexes contain two water molecules in the second sphere linked by hydrogen bonds to each water molecule in the first. When compared with single-sphere models, significant changes are observed for observables such as the uranium-water first-sphere distance, the uranium-"yl" oxygen distance and the uranyl stretching vibrational frequencies. For each of these observables, agreement with experiment is improved by incorporation of the second sphere into the theoretical model. Charge transfer from the solvent to uranyl is substantially enhanced by the second hydration sphere. Effects on these observables of third and subsequent hydration spheres appear to be small, but the influence of water molecules linked to the apical oxygens by a complex hydrogen-bonding network is probably not negligible. Predictions of models based on a polarizable continuum are less satisfactory than those based on an explicit second hydration sphere, particularly for the uranyl vibrational frequencies. Good to excellent linear correlations are observed between charge transfer from the water molecules to the "yl" oxygen atoms, the uranyl bond length and the uranyl stretching frequencies. The inclusion of a second sphere can lead to modifications of the geometry of the first sphere, in particular for the orientation of the water molecules.