

Energetics of Solvated Ions and the Hydrated Electron in Bulk Water and at a Water-Vapor Interface

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Abstract

The vertical binding energies (VBEs) of solvated ions and the hydrated electron in bulk water and at a water-vapor interface have been computed using both resolution-of-identity MP2 and long-range-corrected DFT in conjunction with two continuum solvation models, one of which allows for arbitrary dielectric boundary conditions. Quantitative agreement with recent liquid microjet experiments of VBEs for the bulk species suggests that the chosen methodologies provide reasonable models for solvated ions and excess electrons in water. The VBEs of the interfacial ions and electron are found to be similar to those in the bulk, in contrast to a recent experimental measurement of electron binding energies at a water-vapor interface. Our results provide insight for processes occurring at aqueous-biological interfaces such as dissociative electron attachment to DNA molecules. Crucial to the accuracy of these solvation models is the implementation of dielectric boundary conditions. Therefore we have also investigated how three commonly employed dielectric functions affect computed VBEs as a function of system size.