

Theoretical Studies of the Structure and Spectroscopy of the Hydrated Electron

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Although it is one of the most important radical intermediates in aqueous radiation chemistry, the structure of the aqueous electron has remained controversial. This talk will describe theoretical efforts to model this species, both in the condensed phase and in finite clusters (i.e., negatively-charged water clusters, where the electron-binding motif has also proven controversial). All-electron quantum chemistry calculations are a part of this modeling, but we have also formulated a one-electron atomistic model that takes proper account of electron-water polarization upon excitation or detachment of the hydrated electron. These polarization effects are crucial for quantitative modeling. Our predictions are in quantitative or semi-quantitative agreement with cluster photoelectron spectroscopy, allowing us to make tentative assignments of the observed binding motifs, and furthermore we predict the electron detachment energy in bulk water quantitatively, allowing us to make contact with liquid microjet photoelectron spectroscopy. Simulations of the electronic absorption spectrum provide a means to discriminate amongst various theoretical models, and on the basis of these simulations we put forth an explanation for the "blue tail" in the aqueous electron's near-IR spectrum.