SIMULATING THE PHOTOELECTRON SPECTRA OF HYDRATED-ELECTRON CLUSTERS USING *AB INITIO* MOLECULAR DYNAMICS

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Ab initio molecular dynamics methods are used to simulate photoelectron spectra of small water cluster anions, $(H_2O)_n^-$, including the effects of thermal fluctuations in the geometry of the cluster. Even at temperatures well below 300 K, such fluctuations can significantly alter the vertical electron binding energy (VEBE), and the maximum in the photoelectron intensity distribution typically does not coincide with the VEBE calculated at the minimum-energy geometry. This thermal shift in VEBE can be comparable to, or even large than, the effects of high-level treatments of electron correlation. Simulated photoelectron spectra of $(H_2O)_4^-$ are in quantitative agreement with experiment for molecular dynamics simulations in the range of 150–200 K, and indicate that the experiments probably do not sample a thermodynamic distribution of cluster anions.