ELECTRONIC STRUCTURE STUDIES OF SMALL HYDRATED-ELECTRON CLUSTERS

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Electronic structure calculations reveal common features among small water cluster anions, $(H_2O)_n^-$, with $n = 3$–6. In general, cluster isomers with large electron binding energies are highly unstable on the neutral cluster potential surface, and therefore small changes in the anion geometry can cause large changes in the electron binding energy. Thus the neutral cluster potential surface plays an important role in determining the photoelectron spectrum. Water configurations that are favorable for neutral clusters bind an electron only very weakly, if at all. The global minimum on the $(H_2O)_n$ potential surface is typically lower in energy than any $(H_2O)_n^-$ isomer, meaning that the anionic clusters are metastable with respect to electron autodetachment. Natural bond orbital analysis indicates significant penetration of the unpaired electron into O–H σ^* antibonding orbitals, which explains the large vibrational redshifts observed for $(H_2O)_n^-$, relative to $(H_2O)_n$.