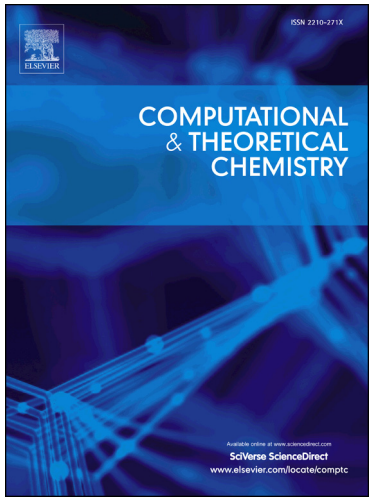

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Atomic Energy Analysis of Cooperativity, Anti-cooperativity, and Non-cooperativity in Small Clusters of Methanol, Water, and Formaldehyde

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Abstract

The local and regional stabilities in clusters of water, methanol, and formaldehyde up to the tetramers have been analyzed from an atomic energy perspective. We optimize structures at the MP2/6-311++G(d,p) level with some CCSD(T)/6-311++G(d,p) single point energies, and then decompose the electronic densities into atomic parts using the atoms in molecules (AIM) approach. We consider the changes in atomic energy in the clusters vs. the isolated monomer. This method of analysis allows us to reveal the variety of stabilities within these hydrogen-bonded clusters, including indications of cooperative, anti-cooperative, and non-cooperative interactions. Cooperatively interacting clusters have increasing stability at the atomic level as the cluster size grows. This is not observed in the anti- and non-cooperative arrangements of water and formaldehyde clusters. The cooperativity in methanol clusters is dominated by the OH regions, with negligible energy change in the methyl regions. Formaldehyde clusters, including the lowest minimum "bucket" cluster, do not show significant cooperativity. Atomic energy analysis is supported with bond critical point data as well as charge and geometric values. We represent the local stability in the clusters using a simple visual approach that allows areas of increased or decreased stability to be easily interpreted.