DFT Evaluations of H_2S Cluster

Jose Mendez, Lisa Bucci, Roger Hall, Gennadiy Beretzuskiy and Glênisson de Oliveira

Rhode Island College, Physical Sciences Department
600 Mt. Pleasant Ave., Providence, RI 02908

Water is one of the most ubiquitous substances in nature, and water clusters are the most studied weakly bound systems. As the second row analog for water, hydrogen sulfide provides an excellent model for our understanding of periodic trends, similarities, and distinctions in the clustering behavior of different substances. Water and H_2S form dimers, trimers, and other small clusters that have very similar molecular orientations. Electrostatics, and quadrupole moments in particular, determine the orientation of these molecules. On the other hand, the nature of the interactions in these clusters differ in that the interaction between water molecules is dominated by electrostatics, while with hydrogen sulfide electrostatics and dispersion have nearly equal contributions to the total interaction. The fact that dispersion plays such an important role in H_2S clusters seems to affect *ab initio* methods, in that the basis set demands on those two types of clusters are different.

We have recently conducted a very extensive comparative study on the use of DFT methods for the evaluation of structures and energetics in water clusters. That was an effort to reproduce results from much more computationally intensive *ab initio* methods, but at a fraction of the cost. Considering the differences in the physical interactions involving water or H_2S, it is important and informative to consider whether the same functionals should be used for hydrogen bonded species and those where dispersion plays a very significant role. Interestingly, the PBE exchange functional yielded the best results when combined with other correlation functionals, and this is certainly different from our results for water clusters.

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