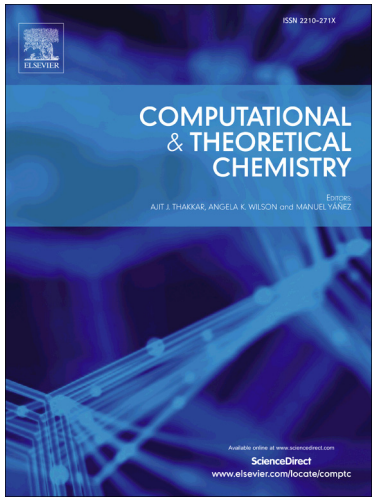

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Density Functional Theory Basis Set Convergence of Sulfuric Acid-Containing Molecular Clusters

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Abstract

We investigate the basis set convergence of three density functionals (M06-2X, PW91, and ωB97X-D) with respect to the binding energy, thermal contribution to the Gibbs free energy, and optimized geometry. We apply correlation consistent, Pople-type, and polarization consistent basis sets with different amount of diffuse and polarization functions. Our test set contains six molecular cluster formation reactions which represent key noncovalent interactions in the atmosphere. In most cases partially augmented basis sets yield as accurate results as the fully augmented basis sets, with significant gain in computational efficiency. Relatively small basis sets are found to be sufficient to optimize geometries and to calculate thermal contributions to the Gibbs free energy. For binding energies, slightly bigger basis sets are needed to reach the complete basis set limit. The PW91 functional with the 6-311++G(3df,3pd) basis set gives a mean absolute error of 0.9 kcal/mol in the binding energy, indicating that it has not reached the complete basis set limit. We estimate the effect of anharmonicity and derive scale factors to correct for it. When the lowest vibrational frequencies are treated separately, the errors arising from the anharmonicity of the remaining frequencies are small regardless of system size. We treated the low frequencies as free rotors and calculate thermal contributions to the Gibbs free energy using the quasi-harmonic approximation. We identify an error of a few percent of the total harmonic thermal contributions, which is larger than the error arising from vibrational anharmonicity.

Keywords: Basis Set Convergence, Density Functional Theory, Molecular Clusters