The performance of Density Functional Theory for Hydrogen Bonded Systems: Shortcomings and Solutions

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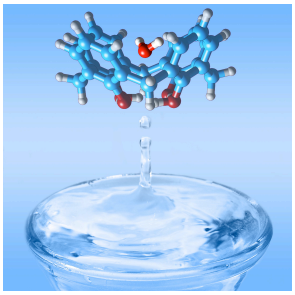
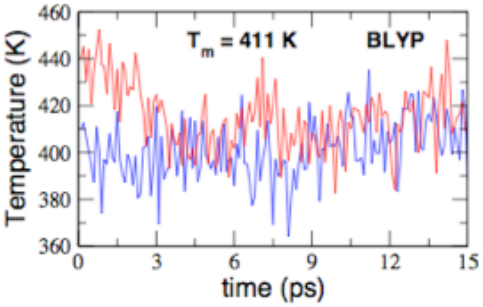
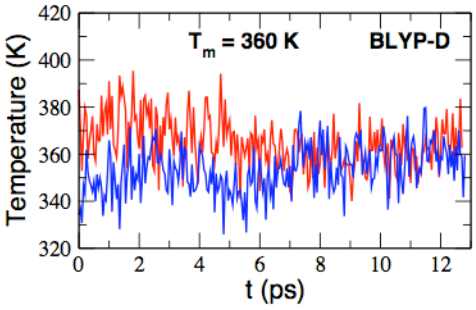
We will present an assessment of the accuracy of various density functionals in describing non-covalent interactions between guest molecules (H_2 H_2O, NH_3, CH_4, C_2H_2) and host functional molecules (calixarenes) (*1*) and the coordination of hydroxide ions in water clusters (*2*). The results of high-level electronic structure calculations at the CCSD(T) level are used as benchmarks to assess the importance of dispersion in recently developed density functionals. We subsequently evaluate the performance of functionals with and without dispersion corrections in describing the melting temperature of liquid water (*3, 4*). Based on these results we rely on a relative-to-the-melting (T_m) rather than an absolute temperature scale for comparing results obtained with various models with experiment. Preliminary results on that relative scale include the 2-D infrared (IR) spectra (*5*) and the anisotropy of liquid water (*6*).







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