

CCSD(T) Complete Basis Set Limit Relative Energies for Low-Lying Water Hexamer Structures

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Abstract

MP2 and CCSD(T) complete basis set (CBS) limit relative electronic energies (ΔE_e) have been determined for 8 low-lying structures of the water hexamer by combining explicitly correlated MP2-R12 computations with higher-order correlation corrections from CCSD(T) calculations. Higher-order correlation effects are quite substantial and increases ΔE_e by at least $+0.19$ kcal mol⁻¹ and as much as $+0.59$ kcal mol⁻¹. The effects from zero-point vibrational energy (ZPVE) have been assessed from unscaled harmonic vibrational frequencies computed at the MP2 level with a correlation consistent triple- ζ basis set (cc-pVTZ for H and aug-cc-pVTZ for O). ZPVE effects are even more significant than higher-order correlation effects and are uniformly negative, decreasing the relative energies by -0.16 to -1.61 kcal mol⁻¹. The prism is consistently the most stable structure, lying 0.06 kcal mol⁻¹ below the nearly isoenergetic cage isomer at the electronic MP2 CBS limit, 0.25 kcal mol⁻¹ at the electronic CCSD(T) CBS limit, and 0.09 kcal mol⁻¹ at the ZPVE corrected CCSD(T) CBS limit. Application of any uniform scaling factor less than unity to correct for anharmonicity further stabilizes the prism and increases the relative energies of the other structures.