

Barriers for Concerted Proton Transfer in the Cyclic Homogeneous Hydrogen-Bonded Trimers, Tetramers and Pentamers of HF, H₂O and HCl at the CCSD(T) Complete Basis Set Limit

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The MP2 and CCSD(T) methods have been paired with correlation consistent basis sets as large as aug-cc-pVQZ to optimize the structures of the cyclic minima for (HF)_n, (H₂O)_n and (HCl)_n, where $n = 3 - 5$, as well as the corresponding transition states for concerted proton transfer. The corresponding harmonic vibrational frequencies confirm the nature of each stationary point. Results for (HF)_n are consistent with prior studies with C_{nh} and D_{nh} point group symmetry for the minima and transition states, respectively. Our computations indicate that the concerted proton transfer processes for the C₁ minima of (H₂O)₃ and (H₂O)₅ minima proceed through C_s transition state structures, whereas the process for the S₄ global minimum of (H₂O)₄ goes through a transition state with D_{2d} symmetry. The minima identified for (HCl)₃, (HCl)₄ and (HCl)₅ have C_{3h}, S₄ and C₁ point group symmetry, respectively. This work also confirms that the C_{nh} structures are not minima for $n = 4$ and 5 . Moreover, our computations show the transition states for concerted proton transfer in (HCl)₃, (HCl)₄ and (HCl)₅ have D_{3h}, D_{2d}, and C₂ point group symmetry, respectively. Canonical and explicitly correlated CCSD(T) computations are being employed to evaluate the barrier heights associated with all 9 concerted proton transfer transition state structures and dissociation energies for all 9 minima near the complete basis set limit.