An efficient two-stage clustering algorithm for probing the potential energy surface of methanol cluster $(CH_3OH)_n$ for n=8-15

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The potential energy surface (PES), structures and the thermal properties of methanol clusters $(CH_3OH)_n$ for n=8-15 were explored by replica-exchange molecular dynamics (REMD) simulations and density functional theory (DFT) methods. For a given size, local minima structures were sampled from REMD trajectories and archived by a newly developed molecular database via a two-stage clustering algorithm (TSCA). Our TSCA utilizes both the topology of O-H...O hydrogen bonding networks and the similarity of the shapes to filter out duplicates. The screened molecular database contains only distinct conformers sampled from REMD and their structures are further optimized by the two DFT methods with and without dispersion correction to examine the influence of dispersion on their structure and binding energy. Inspecting different O-H...O networks, the binding energies of methanol clusters are highly degenerated. The degeneracy is more significant with dispersion effect that introduces complex C-H...O hydrogen bond networks. Most importantly, the possible hydrogen bond networks in liquid methanol were studied systematically using our algorithm, and their correlations to the PES of methanol clusters in different models were revealed.

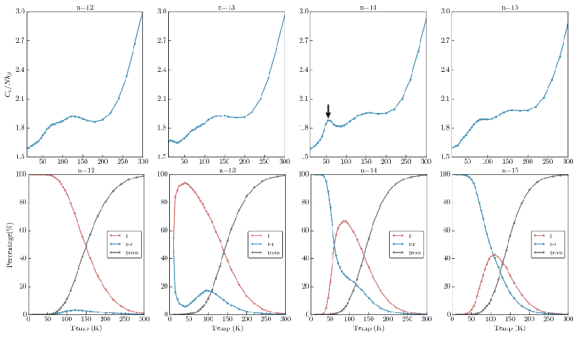

Fig. 1 Heat capacity in reduced and dimensionless form (C_v/Nk_B) (top row) and percentage of the single-ring (r, red line), double-ring (r-r, cyan line), and other topologies involving tree structure (trees, black line) (bottom row) as a function of temperature in $(CH_3OH)_n$ for n=12-15.

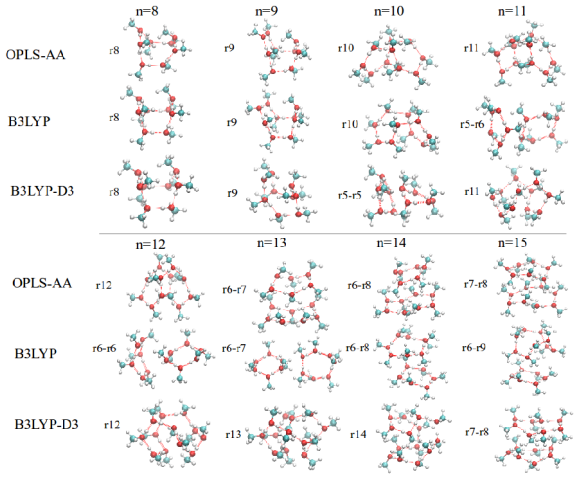

Fig. 2 Global minimum structures of $(CH_3OH)_n$ for n=8-15.