On the three lowest spin states of Na_{13}^+. Hybrid DFT and Benchmark CASSCF(12,12)+CASPT2 studies

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May 19, 2022

Abstract

The three lowest spin states (S=0,1,2) of twelve representative Na_{13}^+ isomers have been studied using both, KS-DFT via three hybrid density functionals, and benchmark multireference CASSCF and CASPT2 methods with a couple of Dunning's correlation consistent basis sets. CASSCF(12,12) geometry optimizations were carried out. Since 12 electrons in 12 active orbitals span the chemically-significant complete valence space, the results of the present study provide benchmarks for Na_{13}^+. The CASPT2(12,12)/cc-pVTZ* lowest energy structures are three nearly degenerate singlets (S=0): an isomer formed from two pentagonal bipyramids fused together (PBPb), a capped centered-squared antiprism [CSAP-(1,3)] and an optimum tetrahedral OPTET(II) structure, the last two lying 0.88 and 1.63 kcal/mol above the first, respectively. The lowest triplet (S=1) and quintet (S=2) states lie 4.33 and 3.77 kcal/mol above the singlet global minimum, respectively. The latter is a deformed icosahedron while the former is a CSAP-(1,3). The flatness of the potential energy surface of this cluster suggests a rather strong dynamical character at finite temperature. Prediction of the lowest energy structures and electronic properties is crucially sensitive both to non-dynamical and dynamical electron correlation treatment. The CASPT2 vertical ionization energy is 3.66 eV, in excellent agreement with the \$3.6 \pm 0.1\$ eV experimental figure. All the isomers are found to have a strong multireference character, thus making Kohn-Sham density functional theory fundamentally inappropriate for these systems. Only large multiconfigurational complete active space self-consistent field (CASSCF) wavefunctions provide a reliable zeroth-order description; then the dynamic correlation effects must be properly taken into account for a truly accurate account of the structural and energetic features of alkali-metal clusters.

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