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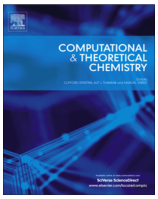

Ab initio investigation of possible candidate structures and properties of water cluster $(H_2O)_7^+$ via particle swarm optimization method

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ABSTRACT

The structures of the ionized water cluster $(H_2O)_7^+$ are investigated through the particle swarm optimization method combined with *ab initio* method. Some new lower energy structures are found after geometric optimization at the MP2/aug-cc-pVDZ level when compared with previous report. We studied the effect of the zero point vibrational energies on the relative energy order of these isomers, the relationship between their schemes and their relative energies, and the composition of their foremost molecular orbitals. The relative free energies of $(H_2O)_7^+$ isomers below 350 K, the infrared spectra of five lowest energy isomers, and their electronic characteristics were discussed in detail, respectively. Based on topological analysis and reduced density gradient analysis, we find that the interaction between H_3O^+ core and water molecules is stronger than the interaction between OH radical and water molecules by comparing the structural and the bonding strengths within these cationic water clusters.

1. Introduction

Water is the source of life on the earth. Without water, most biological processes and chemical reaction cannot take pace [1,2]. Exploring the properties of liquid water can be further promoted by studying water clusters [3–8]. In addition, researchers have found that the ionization of water can occur in a few photocatalytic reactions [9] and some neutron irradiations of cooling water of nuclear atomic plants, which is an important issue for environmental science [10]. To realize microscopic understanding of ionized water, cationic water clusters, whose properties are different from their neutral counterparts, have been a popular subject in recent years [11,12].

The cationic water clusters, monomer $(H_2O)^+$ [13–16] and dimer $(H_2O)_2^+$ [17–20], have been thoroughly investigated in past years. Gardenier et al. [20] found that the structure of dimer $(H_2O)_2^+$ is only the proton-transferred H_3O^+-OH type through IR spectra of the argon-tagged $(H_2O)_2^+$. Up to now, however, the theoretical study of the lager cationic water clusters is still a challenge. There are two reasons for this difficulty. Firstly, the conventional exchange-correlation functionals adopted in density functional theory (DFT) often suffer from some errors [21]. For example, the self-interaction errors make the conventional exchange-correlation functionals give the wrong results for the open-shell dimer $(H_2O)_2^+$ [22–24]. What is worse, as the size of cationic water clusters increases, the local minima on their potential surface increase in the form of exponent [25,26]. The significant breakthrough for larger cationic water clusters has been made in experiment in recent years [27–29]. In 1986, Shinohara et al. [27] found larger cationic water clusters $(H_2O)_n^+$ ($n = 2$–10) for the first time. Haberland and Langosch [28] suggested that $(H_2O)_n^+$ (n = 3–8) can be grown in the cold environment of a supersonic beam. Jongma et al. [29] concluded that the structures of larger cationic water clusters can be understood as a structure of $H_3O^+(H_2O)_{n-1}OH$ with the OH radical situated outside the first solvation shell. This result can be further proved by infrared spectra of water cluster radical cations $(H_2O)_n^+$ ($n = 3$–11) in the gas state, which is measured by Mizuse et al. [30]. The infrared spectra of $(H_2O)_n^+$ ($n = 3$–8) with and without an Ar tag were also observed to get other possible structures [31].

In theoretical respect, some structures of the cationic water clusters $(H_2O)_n^+$ ($n = 2$–4) were obtained by directly optimizing their ionized neutral counterparts at the UHF/4-311++G** level, and their adiabatic ionization potentials were calculated at the MP2 level [32]. The structures of the ionized water clusters, $(H_2O)_n^+$ ($n = 3$–9), were studied by basin hopping search algorithm in combination with density functional theory, second order Møller-Plesset perturbation theory, and coupled cluster theory

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[33]. In addition, researchers also took a great interest in the dynamics and structural change of the cationic water clusters [34]. For example, Lu et al. [35] investigated the structural evolution and solvation of the OH radical in $(H_2O)_n{}^+$ ($n = 5–8$). A series of candidate structures of the cationic water clusters $(H_2O)_n{}^+$ ($n = 4–6$) were researched by the particle swarm optimization (PSO) in combination with *ab initio* method [36,37]. Temelso et al. [38] also investigated the structure and thermodynamics of $H_3O^+(H_2O)_8$ by molecular dynamics and quantum mechanics approach.

However, the studied results for the ionized water cluster, $(H_2O)_n{}^+$ ($n \geqslant 7$), are still unsatisfactory because the structures with the lowest energies have not been confirmed and the information of its properties is still rare. In this work, we focus on water cluster $(H_2O)_7^+$ and present extensive structure searches to explore the structure of its global minimum by CALYPSO [39] combining with *ab initio* methods. The structures were refined and relative energies orders were determined. The Gibbs free energies, vibrational analysis, molecular orbits, and electronic energy gap were also discussed. In the following, we firstly describe the computational methodology in Section 2, and then present our results and discussion in Section 3. Finally, some conclusions are given in Section 4.

2. Computational methodology

The crystal structure analysis via particle swarm optimization code (CALYPSO) [40] was applied to search for as many candidate structures of $(H_2O)_7^+$ as possible. It is tested that the CALYPSO package makes a good performance in cluster prediction [36,37,41]. The particle swarm optimization (PSO) technique utilized in CALYPSO package is inspired by the motion of a bird flock or fish schooling and can be used to perform multidimensional search. Each structure generated by PSO algorithm in the evolution process is affected by either the best local or global structure in the swarm and every individual can learn experience from its past experience to adjust its moving speed and direction. Based on these virtues, the PSO algorithm can get a broad search for the structure efficiently. The thirsty initial structures were randomly generated with certain point group symmetry by CALYPSO code and they were optimized at the HF/6-31G* level by using GAUSSIAN09 package [42]. Seventy percent of the structures with lower energies were evolved into the next generation, where other thirty percent of the structures were again randomly generated. This procedure does not go on until the given criteria are met. In this process, the bond characterization matrix is used to get rid of similar structures, and Metropolis criterion makes the search of cluster structure faster and more efficiently.

The obtained structures of water cluster $(H_2O)_7^+$ with lower energies were refined without any geometry constraint at the MP2/aug-cc-pVDZ level, which is confirmed to rather accurate for different kinds of cationic water clusters [36,37,43–45]. Our calculated positive harmonic vibrational frequencies of these clusters at the level proved that these structures obtained are stable. To improve the accuracy of our calculations, the complete basis set (CBS) limit electronic energies were obtained by the extrapolation scheme without using the nonphysical basis set superposition energy correction (BSSE) [46]. Here, the extrapolation scheme (denoted MP2/CBS) follows the definition: $E_{CBS} = [E_N(N + 1/2)^3$ - $- E_{N-1}(N - 1/2)^3/[(N + 1/2)^3 - (N - 1/2)^3]$, where E_N is the single point energies of isomers obtained at the MP2/aug-cc-pVTZ level and E_{N-1} at the MP2/aug-cc-pVDZ level, and N is three. The zero point vibrational energy (ZPVE) correction used to determine the total energies was made with a scaling factor of 0.9615 [47]. All the calculations were performed in GAUSSIAN09 package [42], and the topological and reduced density gradient (RDG) analysis were carried out by Multiwfn program [48].

3. Results and discussion

3.1. Structure analysis and their energy order

The obtained 15 lower energy structures of water cluster $(H_2O)_7^+$ are shown in Fig. 1. All their structures can be understood as the proton-transferred $(H_3O)^+(H_2O)_{n-2}$ ·OH type. There are no hemi-bonded lower energy structures in our results. According to the structures, we can classify these clusters into five types: the first type is formed by five-membered ring structures (denoted W_1–W_3, W_7, W_9, and similarly hereafter); the second type is the chain-like structure (W_5); the third type is double-four-membered ring structures (W_4, W_8, W_{14}, W_{15}); the forth type is made of a single-four-membered ring structures (W_6, W_{10}, W_{11}, W_{13}); the last type is a cage-like structure (W_{12}). In each same type, all structures only have a subtle difference.

The calculated relative energies E_e (at the MP2/aug-cc-pvdz level) and E'_e (at the MP2/CBS level) with respect to the isomer W_1 are presented in Table 1. It also includes zero point vibrational energy (ZPVE) corrected relative energies E_0 for E_e and E'_0 for E'_e, where ZPVEs are calculated at the MP2/aug-cc-pVDZ level. Fig. 2 illustrates their energy difference. We find that, in the ZPVEs uncorrected case and the ZPVEs corrected case, their relative energies obtained at the MP2/aug-cc-pVDZ level have a distinctively different change trend with subscript number n of isomer W_n. In Table 1, the five structures with lower electronic energies E_e are W_{12}, W_4, W_3, W_1 and W_{14}, but the structures transform to W_1, W_4, W_3, W_2 and W_5 with ZPVE correction. Do and Besley [33] found that the isomer similar with W_5 is the lowest energy isomer by using basin hopping (BH) algorithm and *ab initio* method, whereas Mizuse and Fujii [31] obtained two other lowest energy structures, which are similar to W_5 and W_9 in our results. However, in the ZPVE corrected case, Lu and Pan et al. proposed that the ground state structure is a single four-membered ring, a completely new structure [35]. Hence, it is necessary to calculate more accurate energies of these isomers. In Fig. 2, we show the relative energies E'_0 with ZPVE correction of W_1, W_2, W_3, W_4 and W_5 turn out to be the lowest. This energy order is slightly different from the order, i.e. W_1, W_3, W_2, W_4, and W_6, obtained at the MP2/aug-cc-pVDZ level with ZPVE correction. It is suggested that the isomers W_1, W_2, W_3, W_4 and W_5 have the lowest energies among all isomers obtained. In the following, we adopt the electronic energies obtained at the MP2/CBS level if not specified.

In all the structures, the H_3O^+ cores are directly bonded to three water molecules and separated from OH radical. As a matter of convenience, we here take W_1, W_3, W_7 and W_9 as examples to make a detailed discussion. W_1 is much like W_3. The OH radicals in W_1 and W_3 are bonded to three water molecules and two water molecules, respectively, which result in different dangling O—H band of the terminal two water molecules, and thus W_1 is more stable than W_3. Comparing W_2 with W_7, the relative locations between H_3O^+ cores and OH radicals are different from each other. In W_2, the OH radical sits in the five membered-ring, and in W_7 the OH radical sits in the terminal, thus W_2 and W_7 have different hydrogen bond (denoted HB) strength, and dangling O—H bonds in terminals result in different energies. W_7 and W_9 have the same number HB, but the relationships between H_3O^+ cores and OH radicals are different. In a word, the energies of isomers $(H_2O)_7^+$ are influenced by multi factors, such as HB, dangling O—H bands in water molecules, relative location of H_3O^+ cores, and OH radicals.

The energy difference between a relaxed positively charged compound and the corresponding neutral counterpart, called