

Protonated water clusters

Hartree-Fock study of dissociation energies

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Abstract. A complete set of protonated water clusters conformers up to $n = 8$ have been evaluated by ab-initio Hartree-Fock method in 6-311G** molecular orbitals basis set and with quadratic complete basis set method. Configurations of ground-state conformers are in a good accord with those available in literature but present dissociation energies for the light clusters agree better with experimental values. A tentative analysis of experimental conditions for observation of certain clusters is presented in comparison to selected formation paths of clusters. Dissociation energies show a broad range of values.

1 Introduction

Charged and neutral water clusters are one of the most extensively studied subjects of chemical physics, both theoretically [1–7] and experimentally [8–12]. Small ($n < 6$) protonated clusters were first discovered in low-pressure electrical discharges, see [11] for references. In the liquid phase the pyramidal $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ structure was predicted already by Eigen [13]; the presence of long protonated chains is considered important for unusual properties of the proton transfer in water solutions. In the gas phase at low pressures, charged clusters grow by reactions of water molecules with the H_2O^+ ion, the dominant product in electron-impact ionization. In gas-discharge experiments [11, 14] clusters up to only $n = 7$ were observed, and Kebarle of coworkers [15] observed also $n = 8$. In the lower stratosphere, at temperatures of about 170 K protonated clusters up to $n = 7$ were discovered [16]. At present we check theoretically conditions for the existence of such structures, i.e. formation enthalpies and sketch briefly the possible formation paths.

2 Method

Clusters were optimized by the restricted (i.e. with spin orbitals grouped in pairs) Hartree-Fock (HF) method using the 6.31G* and 6.311G** orbital basis sets, with six d orbitals. The convergence limit of 0.1 kcal/mol was used. For comparison, selected

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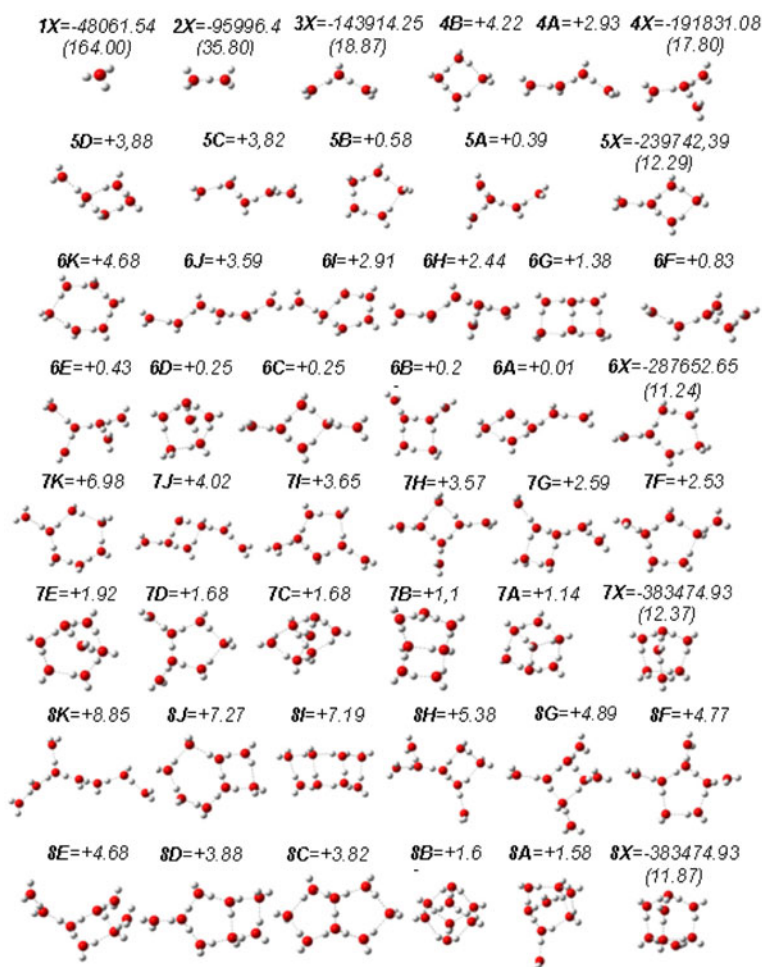


Fig. 1. Geometrical configuration of protonated water clusters family. With X the lowest-laying configurations are labeled with the total electronic energy given and in parenthesis formation enthalpies (in kcal/mol), i.e. the difference between $\text{H}^+(\text{H}_2\text{O})_n + \text{H}_2\text{O}$ and $\text{H}^+(\text{H}_2\text{O})_{(n+1)}$ are given. Numbers by higher-energy configurations state for the difference between total electronic energies of the given and the X state.

structures, like the global minimum-energy (ground) and Eigen's (tree-like) conformers, optimized at the HF/6.311G** level, were additionally evaluated by single-point Møller-Plesset second-order perturbation (MP2) calculations in the 6.311G** basis set. Ground states were also calculated in the HF method using correlation-consistent polarized double zeta (cc-pVDZ) basis set and augmented cc-pVDZ (only up to $n = 4$). Finally the quadratic complete basis set method (CBS-Q) was used to calculate formation enthalpies for all structures of protonated water clusters.

3 Results and discussion

The geometrical configurations of the protonated $\text{H}^+(\text{H}_2\text{O})_n$ clusters family with n up to 8 are given in Fig. 1. Following optical spectroscopy custom, we label with X the lowest-laying state and the A, B, C etc. higher states. Ground states for heavier

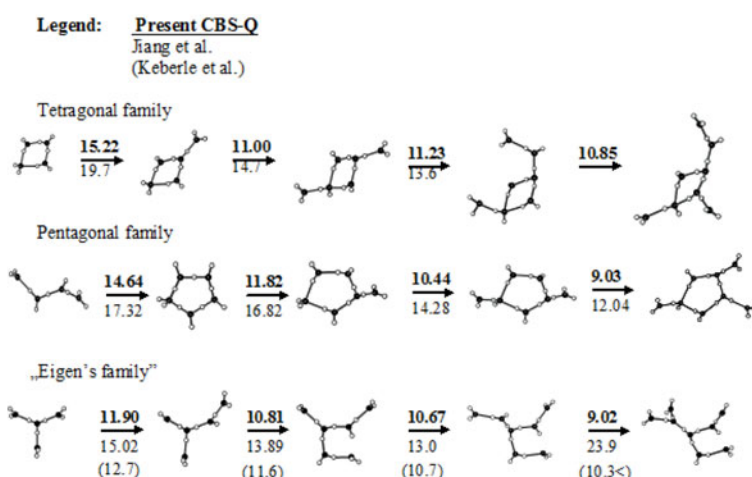


Fig. 2. Formation path for selected protonated water clusters compared with experimental dissociation enthalpies (in kcal/mol).

clusters seem to maximize the number of hydrogen bonds inside the structure. For example, the 7X and 7A conformers contains 9 hydrogen bonds while 7C, 7D lying higher by about 2 kcal/mol contain 8 bonds. However, attempts of excessive bonding of the conformer lead to unstable structures, like in a pentamer a trial to introduce an additional bond by creating a diagonal connection using the “dangling” H_2O molecule in 5B causes an artificial folding of the structure, see 5E in Fig. 2, with fictitious, more than $5a_0$ long bonds. We note that structures based on similar patterns show close values of total energies. For example, tetragon-based pentamers 5A, 5C and 5D, all them lie 0.2–0.4 kcal/mol above the 5X state. Some exceptions exist, like the 6X and 6J (+6 kcal/mol) pair, in which a strong dependence of the total energy on the position of the additional hydrogen atom is evident.

The general shapes of our ground state configurations in the HF/6-311G** approximation for all cluster up to $n = 8$ coincide with those of Hodges and Wales [2]. Only for $n = 6$ our configuration is slightly different (a flat pentagon) but Hodges and Wales' ground configuration (crossed pentagon) has in our calculations the dissociation energy higher by only 0.2 kcal/mol.

Comparison with an extensive (HF, MP2 and density functional) study [17] for several configurations of neutral clusters up to $n = 10$ shows that $n = 6$ ground-state neutral cluster is cyclic, and our cyclic structure 6G lies 5.6 kcal/mol above the pentamer-based 6X; $n = 7$ neutral cluster is a (pentamer + square)-like, as our 7H (=8.6 kcal/mol above 7X); the $n = 8$ neutral is cubic while a cubic protonated cluster 8C is 3.8 kcal/mol above our inter-crossed, hexagon-based 8X.

4 Formation paths

The enthalpies of specific structures do not constitute solely a sufficient condition for their formation in real gas-phase experiments. Not all transitions are allowed, i.e. only some of the heavier structures can be build-up by adding water molecules. As an example, the 6X structure can not be build-up from the 5X structure as an opening of the 5X ring would be needed. In Fig. 2. we show such possible formation paths and we compare the theoretical formation energies with those measured in experiments.

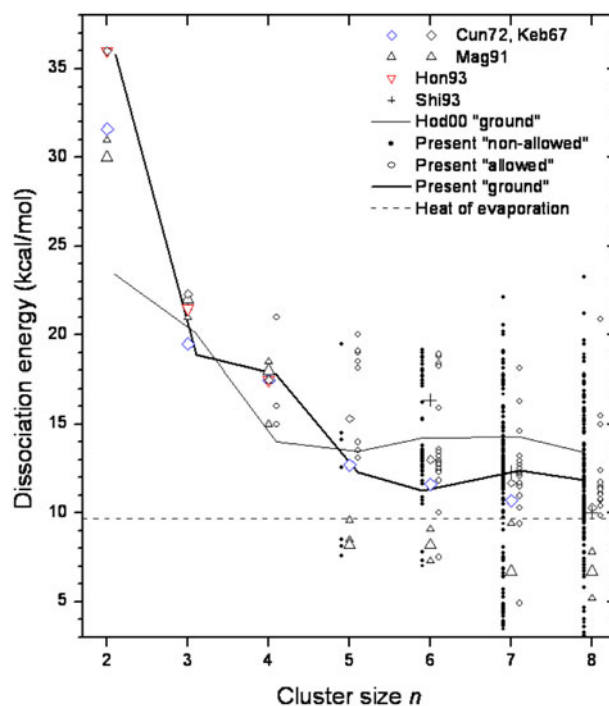


Fig. 3. Formation enthalpies of protonated water clusters; “allowed” states denominate transitions that are topologically possible, i.e. do not require opening of existing bonds.

In Fig. 3, we summarize all possible differences between different geometrical configurations making distinction between “allowed” and “not-allowed” transitions. As seen from Fig. 3, in principle the clusters up to $n = 8$ can be build-up, as their formation enthalpies exceed the heat of water evaporation [18], given as a reference line.

5 Conclusion

The Hartree-Fock and complete basis set methods (CBS-Q) were used for calculations of formation enthalpies of different structures of protonated water clusters containing up to 8 water molecules. In addition to comparison of energetic properties of ground-state conformers with experimental and other theoretical data, the analysis of formation pathways for different “families” of clusters was made. Present results may be helpful in modeling of various physical and chemical processes, such as in the Earth and other planet atmospheres.

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