Small Charged Water Clusters: Cations

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Nonempiric calculation (MP2/UHF/4-31++G**) shows the presence of inherent H_3O and OH fragments in small water cluster cations. According to the arrangement of these fragments, the structures of cations are divided into two groups: either OH fragment acts exclusively as a proton acceptor in all its hydrogen bonds, or it is directly bonded to H_3O and acts also as a proton donor in the H-bond with a water molecule. At the external effect of about 0.4 eV, the former cations can dissociate into free or quasifree OH radical and a protonated water cluster of the corresponding size. An extrapolation of the adiabatic ionization potentials of water clusters to an infinite cluster size provides the value of 8.5 eV close to the experimental photoelectric threshold of amorphous ice. When the adiabatic hydration of the electron knocked out is taken into account, the energy of 6.8 eV should be sufficient for the ionization of an ice specimen.

Introduction

According to most of the known models of liquid water, its structure is ordered to a noticeable degree due to the hydrogen bonds, with certain typical structures prevailing. These may be either fragments of tetrahedral or cubic network or cycles and cages of various configuration. The majority of models predict that five- and six-membered rings should be the most stable and, probably, the most common in liquid water. At the same time, both the predominance of either tetrahedral or cubic arrangement of water molecules in medium-sized clusters and the relative likelihood of cagelike and chainlike configurations are still disputable questions. However, in one or another way, all models imply the existence of small and medium-sized clusters of water molecules. These can be almost free in vapor, but more or less strongly H-bonded in liquid.

The peculiarities in the mutual orientation and interaction of water molecules and their high polarizability are seemingly responsible for the following phenomena. (i) The photoconductivity threshold of ice is almost half of the ionization potential of a water molecule.[1] (ii) Some details of the X-ray structure function of liquid water are typical of ionic and metallic rather than molecular liquids.[2] These experimental facts probably mean that, under appropriate conditions, water clusters may ionize and, in this way, participate in the charge-transfer processes.

Too little is known about the charged water clusters. Despite numerous works devoted to the hydrated electron,[3−11] one still cannot definitely say what is the smallest stable water anion and what are the conditions necessary for its formation. Substantial attention was paid to the protonated water clusters and hydrated hydroxide ions,[12−22] but nobody knows how are they actually formed in vapor or liquid. As to the positively charged water clusters, they gained practically no attention. There were experimental and nonempirical estimates of the vertical[23−26] and adiabatic[26−29] ionization potentials of monomer and dimer; whereas for larger $(H_2O)_n$ clusters ($n = 3$–8), only tentative and relatively rough estimates of the vertical ionization potentials were obtained.[30]

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That is why we analyzed small (comprising to six molecules) neutral and charged water clusters in a consistent approximation, and in this paper, the cluster cations are considered.

Approach Applied

The structures of cations were optimized at the unrestricted Hartree−Fock level (UHF) with the 4-31G basis set augmented with diffuse and polarization functions on all nuclei (4-31++G**). Polarization functions are necessary for obtaining pyramidal structure of H_3O^+ ion,[30] whereas in the absence of diffuse functions, the tendency of the terminal OH fragment (which, as we show below, is inherent in water cations) to separate from the residual structure is not reproduced.[30] The energy characteristics of the HF-optimized structures were estimated in the second order of the Möller−Plesset perturbation theory (MP2). The energy difference between the optimized dimer cation and the cation with the optimal geometry of neutral dimer is almost the same at the MP2 and UHF levels: 2.57 and 2.56 eV, respectively.[30] This fact may indicate that the electron correlation is substantial for estimating the absolute stabilization energy of the cation, but is not decisive as regards the geometry optimization.

Results and Discussion

We analyzed the potential energy surfaces (PES) of $(H_2O)_n$ clusters ($n \leq 6$). For the dimer and trimer, the configurations that correspond to the well-known minima of PES were found. In the case of tetramer, we distinguished three stable structures: (**I**) a cycle with an almost S_4 symmetry (global minimum); (**II**) a triangle of water molecules, one of which is H-bonded to the fourth one; and (**III**) a chain. A thorough analysis of the pentamer PES revealed four stable configurations, namely, (**I**) cyclic; (**II**) close to pyramidal; (**III**) cagelike with an almost C_2 symmetry; and (**IV**) chainlike. Having noticed that, at $n \geq 4$, the clusters can exist both in chainlike and cyclic configurations, we concentrated our effort on searching for such structures of hexamer, and definitely identified (**I**) bathlike cyclic and (**II**) chainlike isomers.
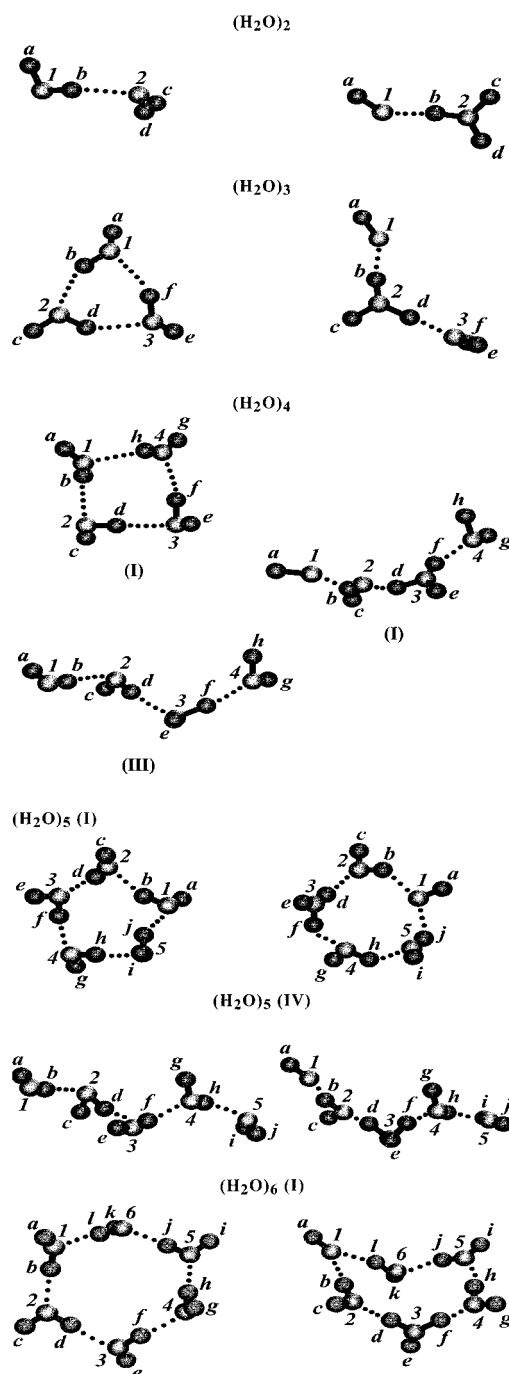
Figure 1. First group structures of water cluster cations (right-hand side) along with the original neutral configurations (left-hand side). Oxygen atoms are denoted as **1**, **2**, etc., while small italic letters are used for hydrogen atoms.

One may consider these neutral structures as possible species in the vapor phase and maybe as distorted parts of the liquid network. Therefore, in the first approximation, the ionization processes can be modeled for these structures. Accordingly, the geometries of cluster cations were optimized with the neutral structures taken as the starting approximation.

In all cations, we can definitely distinguish inherent H_3O and OH fragments. The former looks always like a slightly distorted H_3O^+ ion, while the latter is almost neutral and more or less resembling the OH radical. According to the arrangement of these fragments, the structures of cations were divided into two groups. In one group, OH fragment acts exclusively as a proton acceptor in the H-bonds it forms with the neighbors. These are
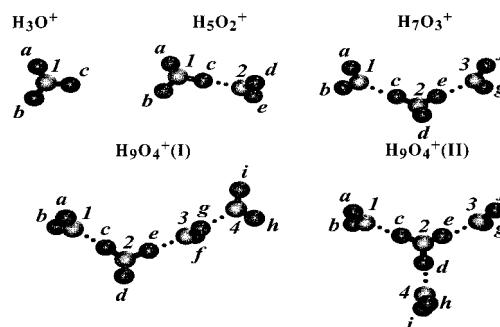

Figure 2. Individual H_3O^+, $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ ions.

chainlike configurations with the terminal OH and the cycles pentamer **I** and hexamer **I**. In the other group, OH is directly bonded to H_3O and acts also as a proton donor in the H-bond with water molecule. Note that, in both groups, one can find both cyclic and chainlike structures.

Let us consider the *first group* (Figure 1). The H_3O fragment is tightly bonded to water molecules. In contrast, the H-bond between OH and neighbor fragments gradually weakens as the cluster increases. This follows from:

(i) The internuclear distances between the O atom of OH and the H atom of the neighbor fragment:

n	2	3	4(**I**)	5(**IV**)	5(**I**)	6(**I**)
$r(O{\cdots}H)$, Å	1.581	1.728	1.947	1.978	2.328, 2.130	2.276, 2.107

(ii) The electron density distribution (atomic charges obtained from the Löwdin population analysis):

n	4(**I**)	5(**IV**)	5(**I**)	6(**I**)
$q(OH)$, au	0.034	0.030	0.033	0.033
$q(H_{2n-1}O_{n-1}^+)$, au	0.966	0.970	0.967	0.967

(iii) The dissociation energies of the cations into OH and the residual structure fragment:

| n	2	3	4(**I**)	5(**IV**)	5(**I**)	6(**I**)
D_e, eV	0.90	0.66	0.41	0.38	0.47	0.45

The dissociation energy was estimated as the energy difference between the optimized cation and its OH and $H_{2n-1}O_{n-1}^+$ fragments, with the counterpoise corrections for the basis set superposition error taken into account.

This peculiarity of the cations means that it is more properly to distinguish only two inherent fragments (or parts) in them, namely, OH and $H_{2n-1}O_{n-1}^+$. To prove this conclusion, we calculated individual H_3O^+, $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ ions (Figure 2). Two possible structures of $H_9O_4^+$ ion were considered: (**I**) a chainlike one, in which one proton of H_3O remains free (i.e., forms no H-bond) and (**II**) a branched one, in which all protons of the central H_3O are H-bonded to water molecules. Only the former structure can be identified in the cations we found. And this is true for both groups of cations, irrespective of the original configuration of neutral cluster. For example, in pentamer **IV**, there is a molecule with tetrahedral coordination, which could produce a three-coordinated hydronium ion. In fact, ionization of this cluster results in a chainlike structure considered below.

The configuration, the electron density distribution, and the dissociation energy of the individual ions are very similar to those of $H_{2n-1}O_{n-1}^+$ fragments. Let us consider all these respects. First, we should note that, in the approximation we use, $H_5O_2^+$ ion is not symmetric. This is a well-known fact, as well as that upon taking into account the electron correlation (e.g., at the configuration interaction (CI) level), the global

TABLE 1: Dissociation Energies (eV) of the Individual $H_{2n-1}O_{n-1}^+$ Ions and the Corresponding Fragments of the First-group Cations

	individual ions				fragments of cluster cations			
species	$H_5O_2^+$	$H_7O_3^+$	$H_9O_4^+$(**I**)	$H_9O_4^+$(**II**)	3	4(**I**)	5(**I**)	5(**IV**)
$E(H_5O_2^+)-E(H_3O^+)-E(H_2O)$	1.60				1.41			
$E(H_7O_3^+)-E(H_3O^+)-2E(H_2O)$		2.44				2.46		
$E(H_9O_4^+)-E(H_3O^+)-3E(H_2O)$			3.14	3.23			3.01	3.10
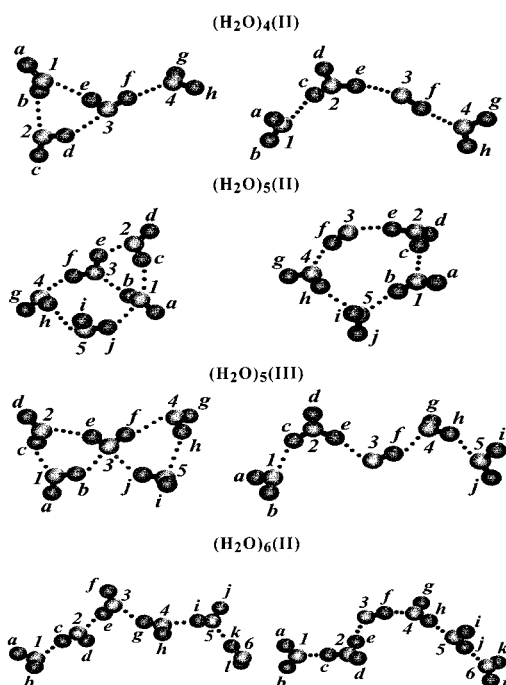
Figure 3. Second group structures of water cluster cations (right-hand side) and the original neutral configurations (left-hand side).

minimum structure becomes symmetric with respect to the central H atom.[19] However, this detail is not principal for the consideration of the protonated water clusters,[31] because for the larger ions, the results obtained at the HF and CI levels agree.

Thus, $H_5O_2^+$ ion is asymmetric and looks like a combination of H_2O and H_3O^+ subspecies. This follows both from the geometric parameters and the electron density distribution: $q(H_3O) = 0.802$ au. $H_7O_3^+$ ion is symmetric with respect to the H_3O fragment, which is easily distinguished in it, with the charge $q(H_3O) = 0.772$ au. This H_3O can definitely be identified in both structures of $H_9O_4^+$. In structure **II**, which is a symmetric pyramid with H_3O at the top, all water molecules are equivalent and have the same charge of 0.088 au. In structure **I,** two molecules directly bonded to H_3O possess higher charges: $q(O^2H^dH^e) = 0.121$ au and $q(O^3H^fH^g) = 0.094$ au, while the third molecule is slightly less charged: $q(O^4H^hH^i) = 0.052$ au.

These features of the protonated species H_3O^+, $H_5O_2^+$, $H_7O_3^+$, and chainlike $H_9O_4^+$ are in agreement with the peculiarities of the $H_{2n-1}O_{n-1}$ fragments: as the cluster increases, a larger part of the positive charge is shared by water molecules, but the charge of each molecule decreases with n and with the increasing distance between the molecule and H_3O fragment in the structure:

n	4(**I**)	5(**IV**)	5(**I**)	6(**I**)
$q(H_3O)$	0.755	0.733	0.732	0.711
$q(O^2H^bH^c)$	0.109	0.086	0.080	0.072
$q(O^4H^gH^h)$	0.102	0.101	0.117	0.130
$q(O^5H^iH^j)$		0.049	0.038	0.030
$q(O^6H^kH^l)$				0.024

Both the isolated ions and the fragments of cations are stable

against dissociation into H_3O^+ ion and water molecules. The estimates of the dissociation energy are given in Table 1. As we can see, these estimates are very close for the species of the same size. This is another argument in favor of considering the cationic clusters as composed of only two inherent fragments, namely, an almost neutral OH and a protonated cluster $[H_3O(H_2O)_{n-2}]^+$. As noted above, the bond between these fragments weakens as the cluster grows, and one can expect that the external effect of about 0.4 eV is sufficient for producing a free or quasifree OH radical and a protonated water cluster of the corresponding size.

Now let us turn to the *second group* of structures (Figure 3). In contrast to the already considered structures, these are characterized by a tight bonding between the OH fragment and the neighbor H_3O and H_2O fragments. This is quite natural, since now OH acts as a proton donor in the H-bond with the water molecule. Hydroxyl has a lower proton affinity (~6.2 eV) than does water molecule (7.14 eV). Therefore, in the individual OH...H_2O complex, it acts as a proton donor.[32,33] The complex itself is not very stable against dissociation into OH and H_2O: $D_e = 5.6$ kcal/mol.[32]

Because of the specific arrangement of OH and H_3O fragments, there are some differences in the electron density distribution in these cations as compared to the first group structures. First of all, the summary charges on OH and H_3O fragments are higher:

	4(**II**)	5(**III**)	5(**II**)	6(**II**)
$q(OH)$	0.058	0.063	0.069	0.069
$q(H_3O)$	0.776	0.752	0.750	0.743

As a consequence, H_2O fragments are almost neutral with the only exception that the charge on the terminal molecule directly bonded to H_3O is of the same order of magnitude as on the H_2O fragments of the first group structures:

	4(**II**)	5(**III**)	5(**II**)	6(**II**)
$q(O^1H^aH^b)$	0.115	0.109	0.096	0.104
$q(O^4H^gH^h)$	0.055	0.039	0.034	0.035
$q(O^5H^iH^j)$		0.036	0.052	0.017
$q(O^6H^kH^l)$				0.030

Another interesting feature of the cations of the second group is that there is a molecule that exclusively acts as a proton acceptor in the H-bonds it forms with the neighbors.

In these structures of cations, one can already find nothing like a protonated water cluster, but the H_5O_2 fragment. For this reason, we cannot speak about more or less probable ways of dissociation. The only correct estimate can be made for the dissociation into all the constituting fragments, namely, OH, H_3O^+, and $(n-2)H_2O$. Compare these estimates for the cations of both groups:

	first group						second group			
n	2	3	4(**I**)	5(**IV**)	5(**I**)	6(**I**)	4(**II**)	5(**III**)	5(**II**)	6(**II**)
D_e, eV	0.90	2.08	2.87	3.48	3.48	3.99	2.71	3.22	3.29	3.99

As one can see, the structures of the first group are slightly more stable.

TABLE 2: Adiabatic Ionization Potentials I_{ad} (eV) of the Neutral Clusters

n	1	2	3	4(**I**)	4(**II**)	4(**III**)	5(**I**)	5(**II**)	5(**III**)	5(**IV**)	6(**I**)	6(**II**)
I_{ad}	12.5	10.7	9.9	9.7	9.5	9.2	9.4	9.4	8.9	9.4	9.2	9.0

To this moment, we considered the probable structures of water cluster cations. An essential question arises on the conditions of their formation. These can be judged from the ionization potentials of the corresponding neutral clusters. This parameter can be estimated as the energy difference between the optimized structure of the neutral cluster and the cationic structure; and depending on which structure of the cation is considered, either optimal or that of the neutral cluster, one obtains either adiabatic or vertical ionization potential. The adiabatic potential is more informative to us, because it takes into account the structural relaxation, which inevitably follows ionization under natural conditions.

The estimated adiabatic ionization potentials (Table 2) of nonchainlike structures almost perfectly fit the straight line:

$$I_{ad} = 8.6 + 3.9(1/n) \qquad (1)$$

where $1/n$ is the reverse number of water molecules in the cluster. Note that the same fitting equation with only minor changes was obtained when either both pentamer and hexamer clusters were not taken into account,[31] or only hexamers were not considered.[32] This fact confirms the validity of the linear dependence

$$I_{ad} - 1/n$$

The potentials of small chainlike clusters are lower than those of the other structures of the same size. This may be accounted for by the fact that, in these structures, the changes that follow the ionization are less substantial, which means that the chainlike structures can be formed more easily. At the same time, they are less stable against dissociation into OH and a protonated cluster, and as such can serve as the main source of the free or quasifree OH radicals.

When the chainlike structures are also taken into account, the approximation equation takes the form

$$I_{ad} = 8.5 + 4.1(1/n) \qquad (2)$$

Equations 1 and 2 provide almost the same value of 8.5 eV for the extrapolated ionization potential of an infinite cluster. This value can be considered as the energy necessary for the ionization of an icelike structure with the removal of an electron to an infinite distance in a vacuum. We considered a diversity of less or more compact configurations of water clusters, and an extrapolation based on these structures should give something like an amorphous ice specimen. In fact, the value of 8.5 eV is very close to the experimental estimate of the photoelectric threshold of amorphous ice: 8.7 ± 0.1 eV.[34] Moreover, if we take into account that, in a real process, the electron knocked out from the neutral cluster is solvated rather than removed to infinity, and recall that, according to ref 35, the adiabatic hydration energy of an electron by water molecules in the bulk should be 1.72 eV, we come to a conclusion that the energy of 6.8 eV is sufficient for the ionization of an ice specimen. This estimate agrees with the observation of ref 1 that the photoconductivity of ice is induced most efficiently by the ultraviolet light with a photon energy of 6.5−6.8 eV.

Conclusions

Nonempiric modeling of the positively charged water clusters shows the probable way of the formation of hydrated protons and OH radicals. The former have typically been studied as individual species, and thus, the problem of their origin has remained unsolved. Both species appear in ice during the irradiation with the ultraviolet light, but the mechanism of the process has not been clear.

Now, we can state that the external effect (e.g., irradiation or impact) with the energy of about 6.8 eV should ionize neutral "clusters" of water molecules in the bulk phase, which always results in the hydrated water clusters and the more or less hydrated (or bound) OH radicals. The electron released is apparently captured by the neighbor water molecules, i.e., solvated. Water anions and the possible state of the excess electron in them are considered in a forthcoming paper.

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