Physical Chemistry

Structural peculiarities and the possibility of the existence of small water cluster anions $(H_2O)_n^-$ with $n \le 4$

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Structures of $(H_2O)_n^-$ anions with $n \le 4$ were optimized at the UHF/4-31++G** level and their stability was estimated at the MP2/4-31++G** level. The trimer anion has a chain-like structure, while the tetramer anion can exist either in a chain-like or a cyclic configuration. In the dimer anion and in the chain-like anions, the excess electron density is localized on the terminal water molecule, an acceptor of the H-bond proton. In the cyclic anion, it is uniformly distributed over the free hydrogen atoms. All considered anions have energy values higher than those of the corresponding neutral oligomers. The detachment of an electron from the anions should proceed with the liberation of energy. However, trimer and larger anions are stable against dissociation into individual water molecules and a free electron.

Key words: water anions, dimers, trimers, and tetramers; stability, dissociation; electron affinity, vertical detachment of an electron; electron density distribution.

Ionization of small $(H_2O)_n$ oligomers with $n \le 4$ results in a substantial change in their structure.[1,2] The following fragments can be distinguished: H_3O^+, $OH^{\cdot}$, and $(n - 2)$ H_2O molecules. According to calculations, H_3O^+ is so strongly bonded to the neighbor water molecules that it is reasonable to consider $H_3O^+(H_2O)_k$ as a single fragment. At the same time, the OH radical is not inclined to hydration and exists either in an almost free form or as a slightly bonded "hydrophobic tail", separated from the H_3O^+ fragment in the $(H_2O)_n^+$ chain with a water molecule. An extrapolation of the calculated adiabatic ionization potentials of the $(H_2O)_n$ oligomers with $n \le 4$ to $n \to \infty$ provides a value of 8.7 eV, which can be considered in certain approximations as the electron work function of liquid water. This result is well supported by the experimental data.[3] Irradiation of ice with UV light with photon energy 6.5—6.8 eV initiates its photoconductivity. Accumulation of hydrogen peroxide in a specimen indirectly confirms the formation of OH radicals.

The calculation results[1,2] provide a new approach to the mechanism and conditions of the ionization of liquid water, and, consequently, to the mechanism of the initiation of photoconductivity. At the same time, it becomes even more necessary to develop a well founded theory of the state of an electron knocked out of the original neutral water cluster. When an electron is captured by a neighbor neutral cluster, what does the formed $\bar{e}(H_2O)_n$ complex look like and how does it participate in the charge transfer process?

Unlike $(H_2O)_n^+$ clusters (instead of which protonated $H^+(H_2O)_k$ clusters have mainly been studied),

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substantial attention[4—12] has been paid to $\bar{e}(H_2O)_n$ clusters. Yet, there is still no clear idea of the size of a cluster able to keep an excess electron, nor of the state of the hydrated electron.

Many experimenters have attempted to obtain negatively charged water clusters in the gas phase. As has been found,[4] a cluster capable of keeping an excess electron must consist of at least 11 H_2O molecules. In experiments with trace amounts of water seeded in an inert gas,[5] practically all $(H_2O)_n^-$ anions with $n \ge 2$ have been obtained. The composition of the ionization products has changed depending on the water content in the inert gas: $(H_2O)_2^-$ formed at 0.1% H_2O; $(H_2O)_n^-$ with n = 6, 7, and ≥10 formed at 2% H_2O; and only $(H_2O)_n^-$ with $n \ge 10$ were observed at 10% H_2O.

The first fairly complete model[6] of the $\bar{e}(H_2O)_n$ complex combined a quantum mechanical description of the excess charge and the first solvation shell with a classical description of the long-range solvent effects. An electron was placed in the center of a tetrahedron formed by four water molecules with the hydrogen atoms directed toward the electron. This $\bar{e}(H_2O)_n$ structure formed the basis for most of the subsequent models. Later[7] a continuous model of the polarizable medium beyond the first hydration shell was replaced with a discrete model where each H_2O molecule was represented by three point charges. In the subsequent works,[8,9] the second solvation layer was modeled by water molecules themselves rather than by the point charges. All the calculation results may be summed up as follows: (1) an excess electron does not attach itself to the existing stable $(H_2O)_n$ cluster when $n \le 12$; (2) to bind an electron, there must be at least two or three layers of water molecules around it; and (3) no anion was found with absolute energy lower than that of the corresponding neutral structure, although at $n \ge 6$ metastable $(H_2O)_n^-$ clusters form that are stable against dissociation into individual water molecules and a free electron. On the whole, these results are in relatively good agreement with the experimental data.

On the question of the localization of the excess electron in a water cluster, the theory and experiment do not agree. The photoelectron spectra of the $(H_2O)_n^-$ clusters allow one to conclude that the electron is localized inside the cluster, because its orbital is predominantly s in type[10] and the energies of vertical detachment of an electron from $(H_2O)_n^-$ anions at n = 11—69 depend linearly on $n^{-1/3}$ (see Ref. 11). In contrast, molecular dynamics calculations with a specially constructed local pseudopotential of the interaction between an electron and a water molecule give the result[12] that, in the case of medium-sized clusters ($8 \le n \le 32$), the attachment of an electron leads to the formation of surface states and only at $n \ge 64$ the inner localization of the electron becomes predominant.

Nevertheless, there is a number of essential questions that remain unanswered. For example, what conditions are necessary for obtaining $(H_2O)_n^-$ structures with $n < 10$, how probable is their formation if there are excess electrons in liquid water, and so on.

These and similar problems may be solved on the basis of, first of all, calculation data. Most of the models are based on constructing an appropriate cavity surrounded by water molecules, in the center of which diffuse s or sp functions are placed to describe the excess electron. This construction is open to doubt. Such functions undoubtedly provide additional possibilities for describing electron localization in liquid water. At the same time, these functions, especially in abundance, can distort results and lead to artifacts. The conclusion that the electron is localized inside a cluster unstable to the detachment of an electron appears to be one such artifact. In the calculations, one typically neglects structure relaxation, though it should follow the introduction of an excess electron into the cluster, usually rigidly fixes the geometry of water molecules, and imposes some symmetry restrictions on the orientation of water molecules.

Method of Calculations

We performed nonempirical calculations of $(H_2O)_n^-$ anions (n = 2—4) without any restriction on the geometry of the water molecules or the symmetry of the whole cluster. The basis involved functions centered only on the nuclei. The $(H_2O)_2^-$ dimer has been thoroughly analyzed, but also with a set of diffuse functions placed at the midpoint between the oxygen atoms.[13] As far as we know, larger anions have not been considered in a similar approximation.

The basis set was chosen for the following reasons. For describing an excess electron, a basis adequate for neutral structures should be augmented with additional functions centered either on the nuclei or between them. The latter variant is typically used. Correspondingly, the result substantially depends on the arrangement and character of these functions. With this in mind, we chose the former approach in which the functions are related to the atoms. Here we possibly underestimate some stabilization effects, but will not obtain nonexistent structures.

It is most obvious and simple to extend a basis set with diffuse functions. However such a basis does not reproduce the features of neutral $(H_2O)_n$ clusters well enough. For this reason, the geometry of the $(H_2O)_n$ and $(H_2O)_n^-$ clusters was optimized with the 4-31++G** basis (*i.e.*, the 4-31G basis set augmented by diffuse and polarization functions on all atoms). The electron correlation energy, which is substantial in the case of anions, was then estimated for the structures that were optimal at the unrestricted Hartree—Fock level. All calculations were performed using the GAMESS program.[14]

All the structures considered correspond to the minima of the potential energy surfaces (PES) and were found as a result of the optimization of the geometry of the $(H_2O)_n^-$ anions. As the initial approximation for the optimization, we used the geometries of the corresponding neutral oligomers, so that the optimized structures of the $(H_2O)_n^-$ anions are essentially the result of the adiabatic relaxation of an oligomer that has gained an excess electron.

All the obtained $(H_2O)_n^-$ anions with $n \le 4$ have absolute energies higher than those of the corresponding neutral oligomers. The vertical detachment energies (*VDE*) of the $(H_2O)_n^-$

anions are negative, which means that these anions are unstable in the absence of stabilizing surroundings. When *n* increases from 1 to 4, the electron affinity of the clusters becomes less negative.

The main tendencies of structural relaxation observed for the small clusters seem to be transferable to larger species as well. Consider now the structures of the $(H_2O)_n^-$ anions. Let us first introduce the abbreviations and designations used for simplifying the discussion. Where it is sufficient for understanding, the chemical symbols of the elements (O and H) are omitted. The O atom is denoted by the italic number that is in parentheses by the O symbol on the figure of the cluster (*e.g.*, *1* instead of O(1)), and the H atom is in the same way denoted by a small italic letter (*e.g.*, *c* instead of H(c)); H_{br} is a hydrogen atom participating in the H-bond ("bridge" atom) and H_{fr} is a "free" atom forming no H-bond; *r*(*1*—*a*) or *r*(*1*...*a*) is the distance between the O(1) and H(a) atoms; θ(*a*—*1*—*b*) is the H(a)—O(1)—H(b) valence angle; φ(*bcd2*) is the H(b)—H(c)—H(d)—O(2) dihedral angle; *q*(*a*) is the charge on the H(a) atom; and *s*(*a*) is the spin population of the H(a) atom. The charges and spin populations were calculated in the framework of Löwdin population analysis.

Results and Discussion

As mentioned above, all the structures correspond to the lowest minima on the potential energy surfaces. $(H_2O)_n^-$ oligomers ($n \leq 4$) are not inclined to bind an excess electron, which is revealed in the positive energy of the corresponding molecular orbital (MO). The energy of this MO is +0.0402 au for the monomer anion and decreases with increasing cluster size (to +0.0129 au for the tetramer anion).

$(H_2O)_n^-$ structures for n = 1—4. The structural peculiarities of the $(H_2O)_n^-$ anions are as follows. Adding an electron to the monomer slightly distorts its structure: the H—O—H valence angle decreases from 107.2° to 104.2°, and the O—H distances increase from 0.943 to 0.950 Å. The excess electron density is distributed mainly on the diffuse s orbitals of the hydrogen atoms, whose population is 0.0152 au in H_2O and 0.4821 au in H_2O^-. The charges and spin populations on the atoms of H_2O^- are as follows (note that in the neutral molecule $q(O) = -0.531$ au and $q(H) = +0.265$ au):

Atom	*q* (au)	*s* (au)
H	−0.201	0.477
O	−0.597	0.045

The geometry of the dimer anion differs substantially from that of the corresponding neutral oligomer (Fig. 1). After the attachment of an electron, the *c2d* molecule, which acts as an acceptor of the H-bond proton, apparently rotates around the axis passing through O(2) and normal to the *a1b* molecular plane. As a result, in contrast to the $(H_2O)_2$ structure, the H(c) and H(d) atoms of $(H_2O)_2^-$ are on the same side of the *12* line as the H(a) atom. Thus, some additional possibilities for localizing the excess electron are acquired, which is confirmed by the composition of the corresponding MO: it involves with comparable weights the diffuse s AOs of the O(2) atom and all the hydrogen atoms.

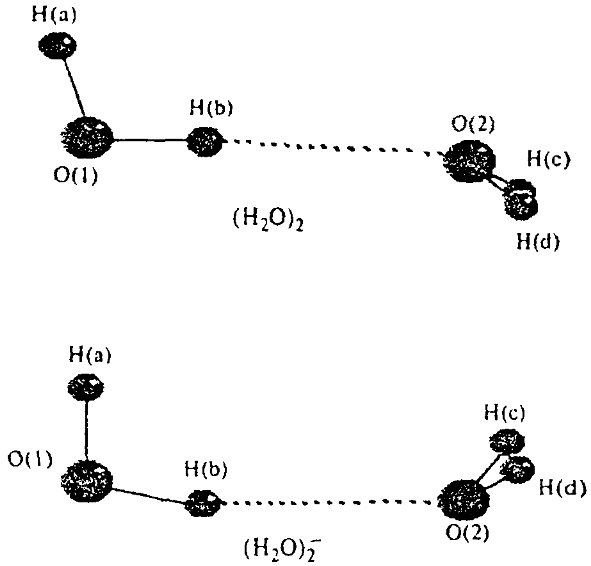

Fig. 1. Structures of the neutral $(H_2O)_2$ dimer and the $(H_2O)_2^-$ anion.

The inner parameters in the *c2d* molecule change in virtually the same way as in the water monomer: the *r*(O—H) distances increase by 0.008 Å (to 0.951 Å), and the valence angle decreases to 104.2°. When there is a similar decrease in the valence angle in the *a1b* molecule, only one O—H distance increases (by 0.006 Å), namely the distance between the O atom and the "bridge" H atom (b). The hydrogen bond itself becomes somewhat less deformed (θ(*1*–*b*...*2*) = 165.9°). The AOs of the *c2d* molecule contribute predominantly to the MO of the excess electron. This is confirmed by the calculated atomic charges and spin populations:

Atom	*q* (au)	*s* (au)
O(1)	−0.572	0.010
O(2)	−0.600	0.062
H(a)	+0.154	0.102
H(b)	+0.253	0.025
H(c)	−0.114	0.396
H(d)	−0.120	0.404

Thus, though judging from the energy of the highest occupied MO of $(H_2O)_2^-$ (+0.0261 au), the dimer has no tendency to bind an excess electron, its structure changes when an electron is brought nearer to it. The excess electron density is localized mainly on that water molecule that acts as a proton acceptor of the H-bond: $q(c2d) = -0.834$ au.

A similar result was obtained in the case of the $(H_2O)_3^-$ anion, though, in the ground state, the neutral water trimer has a cyclic structure, and one could suppose that it would remain so with the addition of an electron. However, the attachment of an electron results in a breaking of the cycle and the formation of a chain-

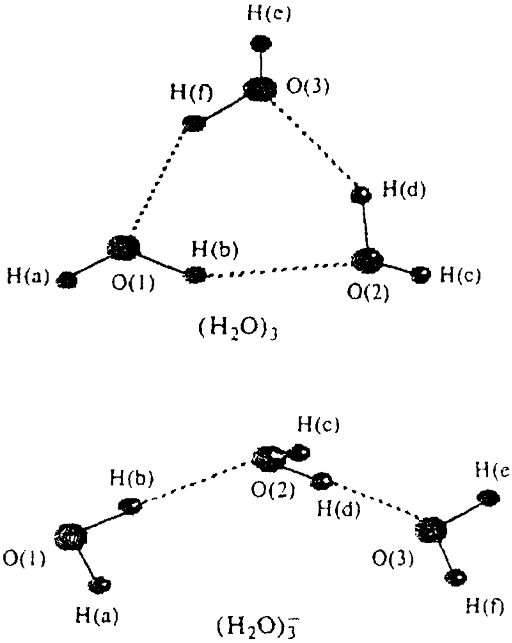

Fig. 2. Structures of the neutral $(H_2O)_3$ trimer and the $(H_2O)_3^-$ anion.

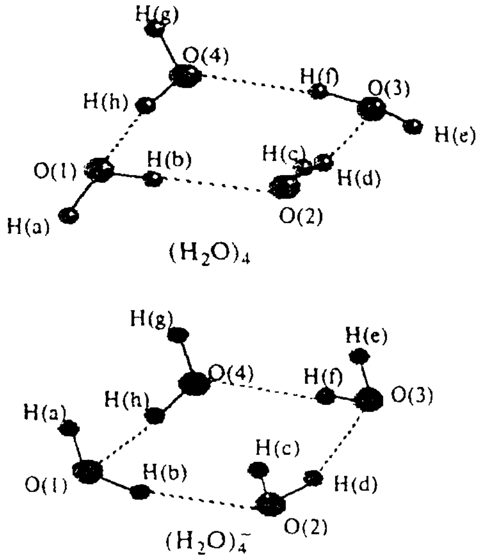

Fig. 3. Structures of the cyclic neutral $(H_2O)_4$ tetramer and the $(H_2O)_4^-$ anion.

like structure (Fig. 2). The neutral tetramer can have either a chain-like or a cyclic structure. Accordingly, after the attachment of an electron, chain-like and cyclic anions form (Figs. 3 and 4).

Chain-like $(H_2O)_3^-$ and $(H_2O)_4^-$ anions look alike. The inner parameters of the constituting H_2O molecules change as follows (Table 1): the H—O—H valence angles decrease on the average by 2.5—3.5°, while the $r(O—H_{fr})$ and $r(O—H_{br})$ distances in the *a1b* and *c2d* molecules of the trimer and in the *a1b*, *c2d*, and *e3f* molecules of the tetramer slightly increase. In the hydrogen bonds, the corresponding $H_{br}...O$ distances decrease. Both the *e3f* molecule of the trimer and the *g4h* molecule of the tetramer undergo almost the same changes as those noted in the monomer and the *c2d* molecule of the dimer. This is confirmed by the charge distribution:

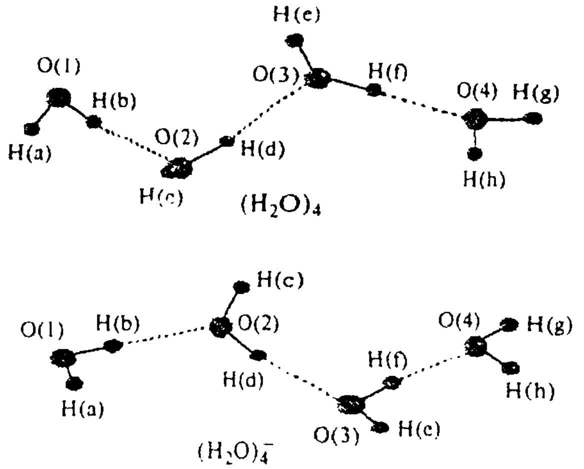

Fig. 4. Structures of the chain-like neutral $(H_2O)_4$ tetramer and the $(H_2O)_4^-$ anion.

in $(H_2O)_3^-$ anion

Atom	*q* (au)	*s* (au)
O(1)	−0.562	0.002
O(2)	−0.567	0.010
O(3)	−0.593	0.062
H(a)	0.238	0.017
H(b)	0.271	0.005
H(c)	0.174	0.089
H(d)	0.259	0.026
H(e)	−0.143	0.430
H(f)	−0.077	0.359

in $(H_2O)_4^-$ anion

Atom	*q* (au)	*s* (au)
O(1)	−0.562	0.000
O(2)	−0.561	0.002
O(3)	−0.566	0.010
O(4)	−0.593	0.060
H(a)	0.255	0.001
H(b)	0.278	0.000
H(c)	0.243	0.020
H(d)	0.278	0.006
H(e)	0.170	0.097
H(f)	0.256	0.032
H(g)	−0.062	0.346
H(h)	−0.135	0.425

Of course, when the number of molecules increases to four, the total "fraction of the negative charge" shared by the other molecules increases somewhat: $q(a1b)$ = −1.0 au in the monomer, $q(c2d)$ = −0.834 au in the dimer, $q(e3f)$ = −0.813 au in the trimer, and $q(g4h)$ = −0.790 au in the tetramer. However, this increase is not so substantial that one could not state that the excess electron density in the anions considered is predominantly localized on one molecule, which is the molecule most deformed compared to its configuration in the original neutral oligomer and is fairly strongly bonded to the residual structure.

Note that on the PES of the trimer anion, we failed to find a minimum that would correspond to a cyclic structure. We found only a definitely pronounced transition state with geometry close to that of the optimized neutral oligomer. The cyclic tetramer anion (see Fig. 3,

Table 1. Comparison of the structures of $(H_2O)_3^-$ and $(H_2O)_4^-$ anions

$(H_2O)_3^-$, chain-like	$(H_2O)_4^-$	
	chain-like	cyclic
	r/Å	
$r(1-a) = 0.943$	$r(1-a) = 0.942$	$r(1-a) = r(3-e) = 0.946$
$r(2-c) = 0.944$	$r(2-c) = r(3-e) = 0.943$	$r(2-c) = r(4-g) = 0.948$
$r(1-b) = 0.952$	$r(1-b) = 0.952$	$r(1-b) = r(3-f) = 0.953$
$r(3-e) = r(3-f) = 0.951$	$r(4-g) = r(4-h) = 0.951$	$r(2-d) = r(4-h) = 0.951$
$r(2-d) = 0.957$	$r(2-d) = r(3-f) = 0.957$	
$r(2...b) = 1.977$	$r(2...b) = 1.974$	$r(1...h) = r(3...d) = 2.075$
$r(3...d) = 1.903$	$r(3...d) = 1.893$	$r(2...b) = r(4...f) = 2.010$
	$r(4...f) = 1.683$	
	θ/deg	
$\theta(1...2...3) = 113.79$	$\theta(1...2...3) = 121.85$	$\theta(1...2...3) = \theta(3...4...1) = 94.34$
	$\theta(2...3...4) = 113.74$	$\theta(2...3...4) = \theta(4...1...2) = 83.41$
$\theta(a-1-b) = 104.87$	$\theta(a-1-b) = 105.31$	$\theta(a-1-b) = \theta(c-2-d) = \theta(e-3-f) = \theta(g-4-h) = 105.24$
$\theta(c-2-d) = 104.75$	$\theta(c-2-d) = 105.78$	
$\theta(e-3-f) = 104.52$	$\theta(e-3-f) = 104.93$	
	$\theta(g-4-h) = 104.64$	
$\theta(1-b...2) = 167.40$	$\theta(1-b...2) = 168.66$	$\theta(1-b...2) = \theta(3-f...4) = 163.77$
$\theta(2-d...3) = 170.43$	$\theta(2-d...3) = 172.08$	$\theta(2-d...3) = \theta(4-h...1) = 161.90$
	$\theta(3-f...4) = 171.64$	
	φ/deg	
	$\varphi(1234) = 132.51$	$\varphi(1234) = -16.14$
$\varphi(a123) = 13.74$	$\varphi(a123) = -29.17$	$\varphi(a123) = \varphi(e341) = 111.74$
	$\varphi(b234) = 135.06$	
$\varphi(c231) = 131.61$	$\varphi(c234) = -11.67$	$\varphi(c234) = \varphi(g412) = 81.29$
	$\varphi(d214) = -42.81$	
$\varphi(e321) = -78.88$	$\varphi(e321) = -106.44$	$\varphi(b143) = \varphi(f321) = -9.58$
	$\varphi(f321) = 127.24$	
$\varphi(f321) = 158.49$	$\varphi(g432) = -156.08$	$\varphi(d214) = \varphi(h432) = 25.66$
	$\varphi(h432) = 81.89$	

Table 1) is geometrically very close to the neutral oligomer: the internuclear distances and valence angles in the H_2O molecules are much the same, and the hydrogen bonds are slightly shorter in the neutral structure. A significant peculiarity of the anion is the arrangement of the free hydrogen atoms: the symmetry of the neutral $(H_2O)_4$ cluster is close to S_4, while that of the $(H_2O)_4^-$ anion is almost C_4. As a result, the two structures of the $(H_2O)_4^-$ anion differ not only in their geometry, but also in their electron density distribution. As mentioned above, in the chain-like structure ~79% of the excess electron density is localized on the terminal H_2O molecule, which is an acceptor of the H-bond proton, whereas in the cyclic structure the excess density is more uniformly distributed over the free H atoms. This observation is confirmed by the relatively high population of diffuse AOs in these atoms (~0.22 au compared to 0.45 au for the 1s AOs of the same atoms).

Energetic characteristics. Estimates of the possibility and conditions of the formation of anions can be made based on the electron affinity of the neutral oligomers. Important here are the characteristics both of the vertical process, *i.e.*, the attachment of an electron to a neutral cluster with fixed geometry (EA_{vert}), and of the adiabatic process, which takes into account the stabilization of the anion due to the subsequent structural relaxation (EA_{ad}). The possibility of the existence of an anion can be judged both from the energy of the vertical detachment of an electron from the anion (*VDE*) and from the stability of the anion to dissociation into individual water molecules and a free electron (*S*).

For calculating these characteristics, one needs fairly correct and consistent estimations of the absolute energies of all the structures in question. This means that the basis set should equally well describe both anions and neutral oligomers. The 4-31++G** basis set we use satisfies this requirement quite well, as it involves both the diffuse functions necessary for the description of an excess electron on anions and the polarization functions, which improve the description of neutral structures. Furthermore, relatively good estimations of the electron correlation energy are obtained by taking into account the second order perturbation theory corrections to the energy (MP2). Table 2 contains the EA_{vert}, EA_{ad}, *VDE*, and *S* values calculated at the MP2/4-31++G** level according to formula

Table 2. Energetic characteristics (eV) of the $(H_2O)_n^-$ anions (n = 1—4)

n	$-EA_{\rm vert}$	$-EA_{\rm ad}$	$-VDE$	S
1	0.973	0.943	0.955	
2	0.705	0.591	0.563	−0.408
3	0.915	0.577	0.328	0.044
4 (chain-like)	0.527	0.276	0.190	0.435
4 (cyclic)	0.888	0.685	0.263	0.437

$$EA_{\rm vert} = E[(H_2O)_n] - E'[(H_2O)_n^-],$$

$$EA_{\rm ad} = E[(H_2O)_n] - E[(H_2O)_n^-],$$

$$VDE = E'[(H_2O)_n] - E[(H_2O)_n^-],$$

$$S = \sum_i E_i(H_2O) - E[(H_2O)_n^-],$$

where $E[(H_2O)_n]$ and $E[(H_2O)_n^-]$ are the absolute energies of the $(H_2O)_n$ and $(H_2O)_n^-$ structures optimized at the UHF/4-31++G** level; $E(H_2O)_i$ $(i = 1, ..., n)$ are the absolute energies of the water molecules constituting a given anion (the calculation was performed with all basis functions of the considered oligomer, *i.e.* with the correction for the basis set superposition error); $E'[(H_2O)_n]$ and $E'[(H_2O)_n^-]$ are the absolute energy of the $(H_2O)_n$ oligomer with the geometry of the optimized anion and that of the $(H_2O)_n^-$ anion with the geometry of the optimized neutral cluster, respectively.

As mentioned above, the vertical attachment of an electron to a small neutral oligomer requires an energy of about 1 eV. The subsequent structural relaxation stabilizes the anion. However, its energy is still higher than those of the optimized neutral oligomer ($EA_{\rm ad}$ is negative, though it decreases in absolute value as n increases) and of the neutral oligomer with the geometry of the optimized anion (the energy of vertical detachment of an electron from the anions is negative, but also decreases in absolute value as n increases; so therefore the chain-like tetramer anion is "more stable" than the cyclic one: the VDE values are −4.4 and −6.1 kcal mol^{-1}, respectively). However, trimer and tetramer anions are stable against dissociation into individual water molecules and an electron (see Table 2). This means that these anions can exist as metastable entities, *e.g.*, in the presence of stabilizing surroundings.

Thus, the calculation of $(H_2O)_n^-$ anions with $n \le 4$ performed in the absence of geometric restrictions and with a basis set that involves only functions centered on the nuclei showed that trimer and tetramer anions have chain-like structures, in which, as in the dimer, the excess electron density is localized mainly on that terminal H_2O molecule that acts as an acceptor of the H-bond proton. The tetramer anion can also exist in a cyclic configuration characterized (compared to the corresponding neutral structure) by a uniform increase in the electron density on the free hydrogen atoms. In all anions, the diffuse s AOs of the H atoms provide the main contribution to the orbital of the excess electron.

All the anions considered have energy values higher than those of the optimal neutral structures and those of the neutral oligomers formed as a result of the vertical detachment of an electron from the anions. However, as n increases, the $EA_{\rm ad}$ and VDE values become less negative. The VDE of the chain-like tetramer is already only −4.4 kcal mol^{-1}, and the anions larger than dimers are stable against dissociation into the constituting water molecules and a free electron. Even in the absence of additional diffuse functions centered between the nuclei, already the trimer anion is metastable. This means that the structural relaxation typically neglected in the calculations[7–9] because of the restrictions imposed on the geometry of individual water molecules and on the symmetry of the whole anion is actually very important. Taking this into account, we obtained new and physically reasonable results.

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