The possibility of the existence of $(H_2O)_n^-$ anions with $n = 5, 6$

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Structural changes that occur in cyclic and chain-like water pentamers and hexamers when an electron is added were analyzed at the unrestricted Hartree—Fock level. The vertical and adiabatic electron affinity of the oligomers, the energies of vertical detachment of an electron from the anions (*VDE*), and the stability of the anions against dissociation into individual water molecules and a free electron were estimated taking into account the second order perturbation theory (MP2) corrections to the energy. All water anions considered are stable against dissociation, but their *VDE* values are negative, and only the chain-like hexamer anion has a value of *VDE* close to zero, which means metastability of the anion. The energy of attachment of an electron to the oligomers is lower in the case of chain-like structures. The process is accompanied by structure relaxation, which is more substantial for cycles, especially for the cyclic hexamer. In the chain-like anions, the excess electron density is localized on the hydrogen nuclei of that terminal water molecule that acts as an acceptor of the H-bond proton, while in the cyclic anions it is distributed on the orbitals of those free hydrogen atoms that significantly approach each other due to structural relaxation.

Key words: water anions, pentamers and hexamers; structure, stability, dissociation; electron affinity, vertical detachment of an electron.

In the previous work,[1] we showed that all models of a hydrated electron described in literature contain some restrictions or assumptions that predetermine the final result. For this reason, we decided to perform nonempirical calculations of the $(H_2O)_n^-$ anions without restrictions on the geometry or orientation of water molecules and with a basis set involving functions centered on the nuclei only. The structures of the $(H_2O)_n^-$ and $(H_2O)_n$ clusters with $n \le 4$ have been optimized[1] at the UHF/4-31++G** level, and the vertical ($EA_{\rm vert}$) and adiabatic ($EA_{\rm ad}$) electron affinity of the $(H_2O)_n$ clusters, the energy of vertical detachment of an electron from the $(H_2O)_n^-$ anions (*VDE*), and the stability of anions against dissociation into individual molecules and a free electron (*S*) have been estimated at the MP2/4-31++G** level.

Though trimer and tetramer anions are stable against such dissociation, vertical detachment of an electron from them proceeds with the liberation of energy. However, as the cluster size increases, this energy decreases so substantially that, if this tendency is retained, the *VDE* value of the hexamer anion could become positive. In the present work we consider $(H_2O)_n^-$ anions with $n = 5$ and 6.

Method of Calculations

As in the previous paper,[1] the O atom is denoted by the italic number that is in the 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)); $H_{\rm br}$ is a hydrogen atom participating in an H-bond ("bridge" atom) and $H_{\rm fr}$ 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; $\theta(a-1-b)$ is the H(a)—O(1)—H(b) angle; $\varphi(bcd2)$ 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. The mean value of some variable f is denoted as $\langle f \rangle$.

All the results were obtained using the GAMESS program.[2]

Results and Discussion

The approach applied. The structures of the $(H_2O)_n^-$ oligomers ($n \le 4$) have been optimized[1] in the framework of the unrestricted Hartree—Fock method with the 4-31++G** basis set, which involves both the diffuse functions necessary for describing the excess electron of anions, and polarization functions, which improve the description of neutral oligomers. Structural optimization of $(H_2O)_n^-$ anions with $n = 5$ and 6 at the same level without geometric restrictions requires too much calculation time. For this reason, we investigated how substantially the structure of anions with $n \le 4$ changes on going from the 4-31++G** basis set to the 4-31++G basis set.

Eliminating polarization functions from the basis set causes no qualitative change as compared to the picture

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 47—53, January, 1997.

1066-5285/97/4601-0042 $18.00 © 1997 Plenum Publishing Corporation

obtained earlier. The parameters of water molecules change in the same way as in the neutral oligomers: the valence angles increase on the average by ~5—5.5°, and in the chain-like trimer and tetramer anions, the least noticeable change is in the valence angle of that terminal water molecule on which the excess electron density is mainly localized. The internuclear distances also increase: $r(O-H_{br})$ on the average by 0.015—0.020 Å and $r(O-H_{fr})$ by 0.007—0.008 Å. As to the hydrogen bonds, the $r(O...H_{fr})$ distances decrease on the average by ~0.2 Å, and the corresponding $\theta(O-H_{br}...O)$ angles increase by ~3° in the dimer, by ~4° in the trimer, by ~3.5° in the chain-like tetramer, and by only ~1.2° in the cyclic tetramer.

The excess electron density in the monomer is still localized mainly on the hydrogen atoms. The charges on these atoms become somewhat less negative (−0.113 au as compared to −0.201 au). In the dimer anion and the chain-like trimer and tetramer anions, the excess density is, as before, distributed over the nuclei of the terminal water molecule. The negative charges, q (au), on the corresponding H atoms are somewhat lower, but on the whole, due to the substantially more negative charge on the O atom, the charge of the molecule is closer to −1 au:

Anion	Charge	UHF/4-31++G**	UHF/4-31++G
$(H_2O)_2^-$	$q(O)$	−0.600	−0.793
	$<q(H)>$	−0.117	−0.050
$(H_2O)_3^-$	$q(O)$	−0.593	−0.794
	$<q(H)>$	−0.110	−0.039
$(H_2O)_4^-$	$q(O)$	−0.593	−0.793
	$<q(H)>$	−0.099	−0.034

Note that the population of the polarization AOs is negligible (~0.04 au) compared to the population of the diffuse s AOs of the H atoms (~0.48 au). In the cyclic tetramer anion, the excess electron density is uniformly distributed over the free hydrogen atoms of all the H_2O molecules. Eliminating the polarization functions from the basis set results in an increase in the charges on the H atoms ($<q(H_{br})>$ from 0.254 to 0.363 au and $<q(H_{fr})>$ from 0.065 to 0.153 au) and a corresponding decrease in the $<q(O)>$ from −0.569 to −0.765 au.

These results allow us to assume that the structural relaxation of water clusters after the attachment of an electron can be studied at the UHF/4-31++G level. The geometric parameters are fairly close to those obtained with the 4-31++G** basis set with only one difference: the strength of the H-bonds is overestimated. As to the electron density distribution, we can sufficiently correctly judge only the contribution from one or another fragment of the cluster anion to the excess electron localization. More precise data can be obtained in a single-point calculation of the UHF/4-31++G-optimal structure with the 4-31++G** basis. We should also estimate how significantly the basis size affects the calculated energetic characteristics.

Table 1 contains estimations of the vertical and adiabatic electron affinity of the neutral oligomers, the energies of the vertical detachment of an electron from the anions, and the stability of the anions against dissociation into separate water molecules and a free electron. The energetic characteristics were calculated taking into account the second order perturbation theory (MP2) corrections to the energy:

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

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

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

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

where $E[(H_2O)_n]$ and $E[(H_2O)_n^-]$ are the absolute energies of the structures of the neutral oligomer and the anion optimized at the Hartree—Fock level; $E'[(H_2O)_n]$ and $E'[(H_2O)_n^-]$ are the absolute energy of the neutral oligomer with the geometry of the optimized anion and that of the anion with the geometry of the optimized neutral oligomer, respectively; and $E_i(H_2O)$ (i = 1,..., n) are the energies of the constituting water molecules corrected for the basis set superposition error. The columns entitled 4-31++G and 4-31++G** contain the energetic estimations obtained using the specified basis set for structures optimized with that basis. The "4-31++G**" columns contain the energetic estimations obtained using the 4-31++G** basis set for structures optimized with the 4-31++G basis.

Consider the energies of vertical detachment of an electron from the cluster anions and their stability against

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

n	$-EA_{vert}$			$-EA_{ad}$			$-VDE$			S		
	I	II	III	I	II	III	I	II	III	I	II	III
1	0.957	0.973	0.981	0.916	0.943	0.932	0.931	0.955	0.959			
2	0.640	0.705	0.689	0.536	0.591	0.589	0.532	0.563	0.600	−0.312	−0.408	−0.448
3	1.017	0.915	0.979	0.578	0.577	0.536	0.279	0.328	0.360	0.226	0.044	0.002
4 (cyclic)	0.991	0.888	0.948	0.879	0.685	0.593	0.450	0.263	0.533	0.553	0.437	0.363
4 (chain-like)	0.343	0.527	0.407	0.171	0.276	0.269	0.143	0.190	0.228	0.711	0.435	0.389

Note. I, 4-31++G; II, 4-31++G**; III, "4-31++G**".

dissociation into the constituting water molecules and an electron. These values determine the possibility of the existence of the anions. The calculations with the 4-31++G basis set underestimate the "instability" of the anions, while those in the "4-31++G**" variant overestimate it. The 4-31++G basis set involves diffuse functions, which are necessary for reproducing the stabilization effects of the anions, but it does not correctly describe some of the structural peculiarities of the neutral oligomers. Therefore, the estimations of *VDE* and *S* with the 4-31++G basis set are somewhat higher than those with the 4-31++G** basis. At the same time, in the "4-31++G**" variant, the energy of an anion is not minimum, because the optimization has been performed in the absence of polarization functions, and, correspondingly, the *VDE* and *S* values are lower than those obtained with the 4-31++G** basis set. Thus, the "real" estimations (with the 4-31++G** basis set) lie somewhere between those obtained in the 4-31++G and "4-31++G**" variants.

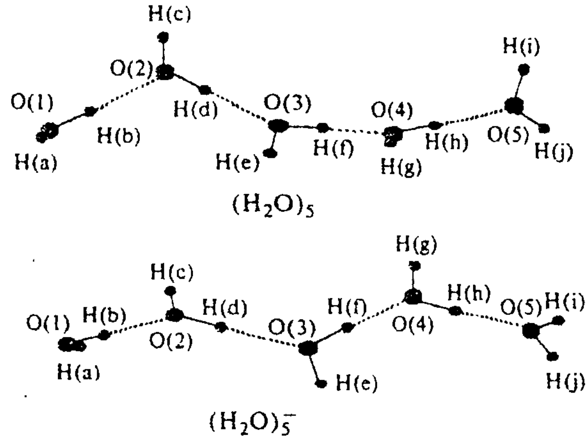


Fig. 1. Structures of the chain-like neutral $(H_2O)_5$ pentamer and the $(H_2O)_5^-$ anion.

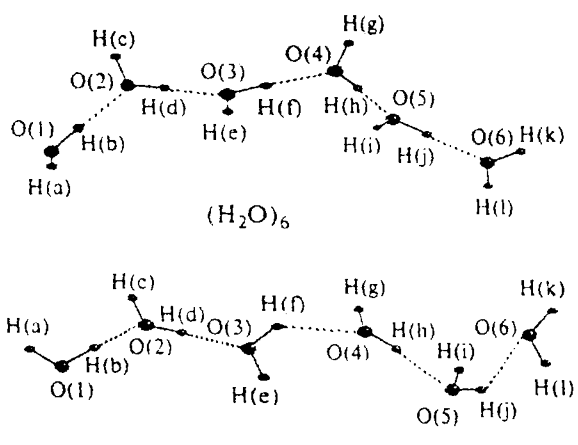


Fig. 2. Structures of the chain-like neutral $(H_2O)_6$ hexamer and the $(H_2O)_6^-$ anion.

Thus, the optimization of the geometry of $(H_2O)_n^-$ clusters with $n = 5$ and 6 can be performed at the UHF/4-31++G level, and the electron density distribution in the obtained structure can be estimated in a single-point run with the 4-31++G** basis set. The stability of the structures can be judged from the upper (MP2/4-31++G) and lower estimations (MP2/"4-31++G**") of the *VDE* and *S* values.

$(H_2O)_n^-$ structures (n = 5, 6). All structures considered below correspond to minima on the potential energy surfaces. Pentamer and hexamer anions, similarly to the tetramer anion, can exist not only in a cyclic configuration, but also as, among others, chain-like structures (Figs. 1—4).

The geometric parameters of the chain-like pentamer and hexamer anions (see Figs. 1 and 2) are compared in Table 2. Structurally, they differ insignificantly from the original neutral oligomers. The parameters of the individual water molecules, their mutual orientation, and the strength of the H-bonds between them are similar in these chains. The hydrogen bonds are somewhat shorter and less deformed than those in the neutral oligomers. The excess electron density is localized chiefly on the terminal H_2O molecule that is an acceptor of the H-bond proton: $q(5ij) = -0.830$ au in the pentamer anion and $q(6kl) = -0.817$ au in the hexamer anion. Accordingly, the greatest contributions to the highest occupied MO come from the diffuse s orbitals of the H(i), H(j), O(5), and H(h) atoms in the case of the pentamer anion and

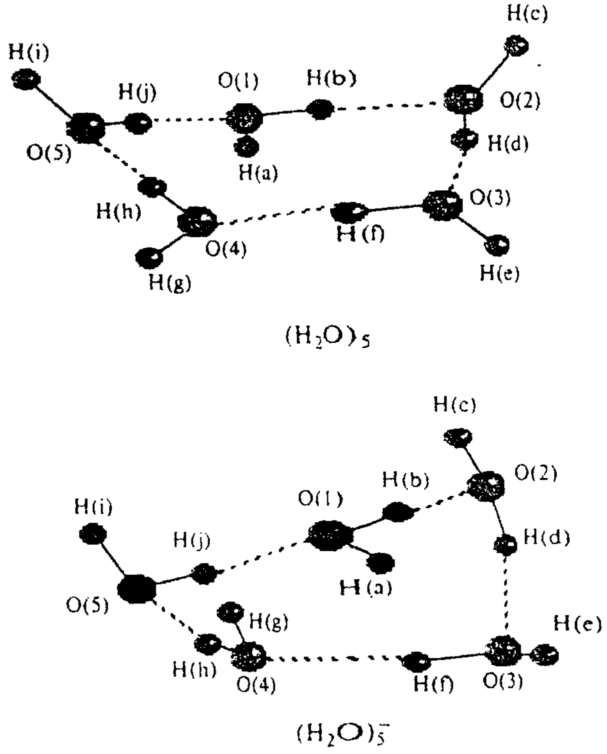
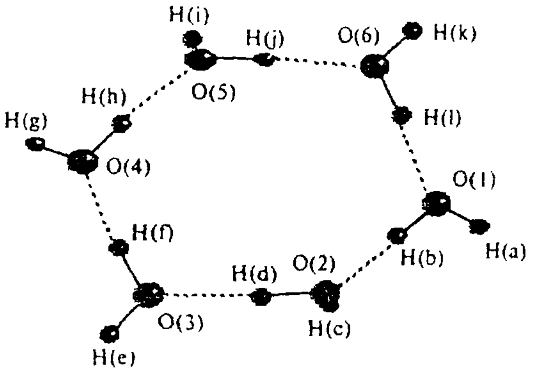
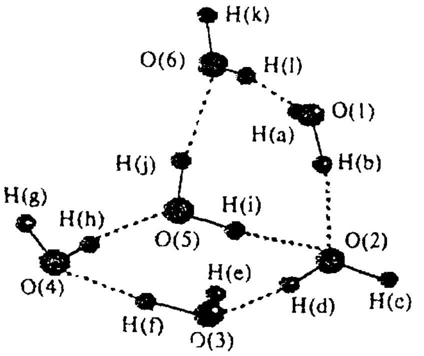


Fig. 3. Structures of the cyclic neutral $(H_2O)_5$ pentamer and the $(H_2O)_5^-$ anion.



$(H_2O)_6$



$(H_2O)_6^-$

Fig. 4. Structures of the cyclic neutral $(H_2O)_6$ hexamer and the $(H_2O)_6^-$ anion.

from the H(k), H(l), O(6), and H(j) atoms in the case of the hexamer anion. Note, however, that the energy of this MO is positive: 0.0057 au in $(H_2O)_5^-$ and 0.0031 au in $(H_2O)_6^-$.

The cyclic pentamer and hexamer anions are less similar in structure and charge distribution, and do not resemble the tetramer anion. Consider first the pentamer (Table 3, see Fig. 3). Both in the neutral oligomer and in the anion, four oxygen atoms lie practically in the same plane, but the deviation of the fifth oxygen atom (O(2)) from this plane is substantially larger in the anion. On the whole, the excess electron makes the structure more compact, because the molecules reorient to provide the maximum possible localization of the excess electron density. Therefore the most distant fragments of the structure approach each other: in the neutral cluster, $r(c\ldots g)$ = 5.670 Å and $r(c\ldots i)$ = 5.732 Å, while in the anion, $r(c\ldots g)$ = 3.932 Å and $r(c\ldots i)$ = 4.276 Å. As a result, the greatest contribution to the highest occupied MO comes from the diffuse s orbitals of the H(c), H(g), and H(i) atoms. Accordingly, compared to the neutral oligomer, the charges on the H(c) and H(g) atoms change most substantially, and those on the H(i) and H(e) change less noticeably: $q(g)$ = −0.043 au, $q(c)$ = 0.050 au, $q(i)$ = 0.144 au, and $q(e)$ = 0.150 au. The charges on the other hydrogen atoms are on the average 0.270 au and $\langle q(O)\rangle = -0.584$ au. For comparison, in the neutral pentamer, $\langle q(H_{fr})\rangle$ = 0.269 au, $\langle q(H_{br})\rangle$ = 0.297 au, and $\langle q(O)\rangle$ = −0.566 au.

Table 2. Geometric parameters of the chain-like pentamer and hexamer anions

$(H_2O)_5^-$	$(H_2O)_6^-$
r/Å	
$r(1{-}a) = r(2{-}c) = r(3{-}e) = r(4{-}g) = 0.949$	$r(1{-}a) = r(2{-}c) = r(3{-}e) = r(4{-}g) = r(5{-}i) = 0.949$
$r(1{-}b) = 0.967$	$r(1{-}b) = 0.966$
$r(2{-}d) = r(3{-}f) = r(4{-}h) = 0.976$	$r(2{-}d) = r(3{-}f) = r(4{-}h) = r(5{-}j) = 0.976$
$r(5{-}i) = r(5{-}j) = 0.962$	$r(6{-}k) = r(6{-}l) = 0.962$
$r(2\ldots b) = 1.779$	$r(2\ldots b) = 1.783$
$r(3\ldots d) = 1.692$	$r(3\ldots d) = 1.709$
$r(4\ldots f) = 1.679$	$r(4\ldots f) = 1.673$
$r(5\ldots h) = 1.673$	$r(5\ldots h) = 1.680$
	$r(6\ldots j) = 1.668$
θ/deg	
for a1b, c2d, e3f, and g4h:	*for a1b, c2d, e3f, g4h, and i5j:*
$\langle\theta(H{-}O{-}H)\rangle = 111.53$	$\langle\theta(H{-}O{-}H)\rangle = 111.62$
$\theta(i{-}5{-}j) = 109.39$	$\theta(k{-}6{-}l) = 109.47$
for 1—b...2, 2—d...3, 3—f...4, and 4—h...5:	$\theta(1{-}b\ldots 2) = \theta(4{-}h\ldots 5) = 172.71$
	$\theta(2{-}d\ldots 3) = \theta(5{-}j\ldots 6) = 178.36$
$\langle\theta(O{-}H\ldots O)\rangle = 175.84$	$\theta(3{-}f\ldots 4) = 175.57$
$\theta(1\ldots 2\ldots 3) = 130.00$	$\theta(1\ldots 2\ldots 3) = 127.33$
$\theta(2\ldots 3\ldots 4) = 128.45$	$\theta(2\ldots 3\ldots 4) = 129.72$
$\theta(3\ldots 4\ldots 5) = 121.77$	$\theta(3\ldots 4\ldots 5) = 131.40$
	$\theta(4\ldots 5\ldots 6) = 115.63$
φ/deg	
$\varphi(a123) = 43.79$	$\varphi(a123) = -75.59$
$\varphi(c234) = 72.12$	$\varphi(c234) = -16.34$
$\varphi(e345) = 13.60$	$\varphi(e345) = 64.89$
$\varphi(g432) = 20.14$	$\varphi(g456) = 15.14$
	$\varphi(i543) = 31.72$
$\varphi(i543) = 97.46$	$\varphi(k654) = 94.12$
$\varphi(j543) = -85.30$	$\varphi(l654) = -82.82$
$\varphi(b234) = -113.02$	$\varphi(b234) = 174.33$
$\varphi(d345) = -169.12$	$\varphi(d345) = -121.29$
$\varphi(f321) = -110.83$	$\varphi(f321) = 168.61$
$\varphi(h432) = -166.49$	$\varphi(h432) = -119.86$
	$\varphi(j543) = -154.96$

In the cyclic hexamer, similar changes that occur when an electron is added are still more pronounced (Table 4, see Fig. 4). The *i5j* and *c2d* molecules approach each other so that an H-bond is formed between them: in the neutral hexamer $r(2\ldots 5)$ = 4.667 Å, whereas in the anion $r(2\ldots 5)$ = 2.884 Å. As a result, the oxygen atoms of $(H_2O)_6^-$ form two quadrangles (*2345* and *1256*) with a common side that are practically planar

Table 3. Geometric parameters of the cyclic water pentamer and pentamer anion

Parameter	$(H_2O)_5$	$(H_2O)_5^-$
	r/Å	
$\langle r(\mathrm{O{-}H_{fr}})\rangle$	0.948	0.952
$\langle r(\mathrm{O{-}H_{br}})\rangle$	0.973	0.971
$\langle r(\mathrm{O...H_{br}})\rangle$	1.700	1.768
	θ/deg	
$\langle\theta(\mathrm{H{-}O{-}H})\rangle$	113.23	111.65
$\langle\theta(\mathrm{O{-}H_{br}...O})\rangle$	171.76	169.04
θ(*1...2...3*)	103.22	102.54
θ(*2...3...4*)	105.32	91.54
θ(*3...4...5*)	106.66	109.84
θ(*4...5...1*)	105.88	100.18
θ(*5...1...2*)	105.82	98.38
	φ/deg	
φ(*a154*)	−128.38	−104.68
φ(*c215*)	112.68	58.98
φ(*e321*)	−110.98	175.97
φ(*g432*)	141.09	79.51
φ(*i543*)	168.77	119.12
φ(*1234*)	35.11	57.92
φ(*2345*)	−22.48	−36.57
φ(*3451*)	0.94	4.66

and normal to each other. Judging from the charges, the excess electron density is localized predominantly on the H(a) and H(e) nuclei (most distant in the neutral structure), and is localized to a lesser degree near the H(g) and H(c) nuclei: $q(a) = -0.053$ au, $q(e) = -0.036$ au, $q(g) = 0.203$ au, and $q(c) = 0.215$ au. The charges of the other H atoms equal on the average 0.272 au, and $\langle q(\mathrm{O})\rangle = -0.585$ au. The greatest contribution to the expansion of the highest occupied MO comes from the diffuse s AOs of the H(a) and H(e) atoms. The excess electron density causes the molecules most distant in the neutral structure to reorient and significantly approach each other: in $(H_2O)_6$ $r(a...g) = 6.589$ Å and $r(a...e) = 5.831$ Å, whereas in the anion $r(a...g) = 4.510$ Å and $r(a...e) = 3.718$ Å.

Thus, a distinguishing peculiarity of the cyclic hexamer anion is the H-bond between the *i5j* and *c2d* molecules, which additionally stabilizes the structure. Though the character of the localization of the excess electron density does not provide a positive electron affinity for the given cycle, it probably shows under which conditions this may occur. This question will be discussed more precisely after modeling the octamer. Judging from the structures of $(H_2O)_5^-$ and $(H_2O)_6^-$, the cyclic octamer anion would have an almost cubic structure, and the excess electron density would be localized on the AOs of the free hydrogen atoms. Depending on the orientation of these atoms (inside or outside the cube), one would be able to conditionally name the localization either inner or surface.

Thus, nonempirical calculation of the $(H_2O)_n^-$ structures with $n \le 6$ without geometric restrictions and with a basis set involving only functions centered on the atoms provides interesting results that differ essentially from those published earlier[3–6]. By introducing additional diffuse functions centered between the nuclei, one may imitate additional stabilization of these structures. However, one should first prove that the chosen number and arrangement of the functions do not lead to artifacts.

Let us turn now to the problem of the existence and stability of anions of the water oligomers. As can be seen from Table 5, both the vertical and adiabatic electron affinities of the chain-like oligomers are substantially less negative than those of the cyclic oligomers. Taking into account that, when compared to the MP2/4-31++G** calculation, both the MP2/4-31++G and MP2/"4-31++G**" calculations underestimate to some extent (in absolute value) the electron affinity of chain-like structures (see Table 1), we may assume that EA_{vert} and EA_{ad} of the chain-like hexamer are about −0.35 eV (or −8.1 kcal mol^{-1}) and −0.15 eV (or −3.5 kcal mol^{-1}), respectively. This means that $|EA_{\mathrm{vert}}|$ of the hexamer does not exceed in order of magnitude the energy of the hydrogen bond, while $|EA_{\mathrm{ad}}| \sim kT$ at room temperature. Consequently, the formation of the anion of the chain-like hexamer is thermodynamically probable; but can this structure exist?

Experimentally, water cluster anions with less than 10 molecules have been obtained[7,8] only by seeding trace amounts of water in a supersonic beam of inert gas and introducing low-energy electrons into the condensation zone of the beam. This means that either an anion of this size has an absolute energy higher than that of the neutral oligomer of the same geometry, or the energy gap between such an anion and the corresponding neutral oligomer does not exceed the excitation energy typical of a supersonic beam. The actual reason can be judged from the *VDE* value, *i.e.*, from the energy of the vertical detachment of an electron from the cluster anion. As noted above, calculations in the MP2/4-31++G and MP2/"4-31++G**" variants provide the upper and lower boundaries of the value in question. Obviously, the *VDE* is positive for both pentamer anions and for the cyclic hexamer anion (see Table 5), but it approaches zero in the case of the chain-like hexamer anion, which means that this anion is already metastable. This estimate is in agreement with the experimental data,[9] according to which the *VDE* of the hexamer anion is a small (~3 kcal mol^{-1}) positive value (the VDE—$n^{-1/3}$ curve intersects the $n^{-1/3}$ axis near $n = 6$).

Judging from the absolute energies, the anions of the cyclic water oligomers are thermodynamically more stable than those of the corresponding chain-like isomers. However, the former differ geometrically much more from the corresponding equilibrium neutral oligomers.

Table 4. Geometric parameters of the cyclic water hexamer and the hexamer anion

$(H_2O)_6$	$(H_2O)_6^-$
r/Å	
for $\alpha\beta$ = *12, 23, 34, 45, 56, and 61*: $\langle r(\alpha...\beta)\rangle = 2.664$	*for* $\alpha\beta$ = *12, 23, 34, 45, 56, 61, and 25*: $\langle r(\alpha...\beta)\rangle = 2.761$
$r(2...5) = 4.667$	
$\langle r(O-H_{fr})\rangle = 0.948$	$r(1-a) = r(3-e) = 0.956$
	$r(2-c) = r(4-g) = r(6-k) = 0.949$
$\langle r(O-H_{br})\rangle = 0.974$	$r(1-b) = r(3-f) = r(5-j) = r(5-i) = 0.963$
	$r(4-h) = r(6-l) = 0.973$
	$r(2-d) = 0.980$
$\langle r(O...H_{br})\rangle = 1.693$	$r(1...l) = r(3...d) = 1.692$
	$r(5...h) = 1.786$
	$r(4...f) = r(6...j) = 1.850$
	$r(2...b) = 1.892$
	$r(2...i) = 1.976$
θ/deg	
for $\alpha\beta\gamma$ = *123 and 456*: $\langle\theta(\alpha...\beta...\gamma)\rangle = 116.74$	*for* $\alpha\beta\gamma$ = *123, 234, 345, 456, 561, 612, 125, 256, 452, and 523*: $\langle\theta(\alpha...\beta...\gamma)\rangle = 91.1$
for $\alpha\beta\gamma$ = *234, 345, 561, and 612*: $\langle\theta(\alpha...\beta...\gamma)\rangle = 111.67$	
$\langle\theta(H-O-H)\rangle = 112.89$	$\langle\theta(H-O-H)\rangle = 112.10$
$\theta(1-b...2) = \theta(4-h...5) = 177.19$	$\theta(3-f...4) = 161.32$
$\theta(2-d...3) = \theta(5-j...6) = 175.99$	$\theta(1-b...2) = \theta(2-d...3) = 169.38$
$\theta(3-f...4) = \theta(6-l...1) = 174.04$	$\theta(4-h...5) = \theta(6-l...1) = 166.57$
	$\theta(5-j...6) = \theta(5-i...2) = 157.39$
φ/deg	
$\varphi(1256) = -6.49$	$\varphi(1256) = -17.13$
$\varphi(2345) = -13.32$	$\varphi(2345) = -3.58$
$\varphi(a165) = 153.01$	$\varphi(a165) = 112.10$
	$\varphi(b165) = -22.05$
$\varphi(c216) = -94.36$	$\varphi(c216) = -126.28$
	$\varphi(d254) = -7.56$
$\varphi(e321) = 131.02$	$\varphi(e345) = -122.20$
	$\varphi(f325) = -0.10$
$\varphi(g432) = 147.56$	$\varphi(g432) = 109.30$
	$\varphi(h432) = -7.02$
$\varphi(i543) = -93.91$	$\varphi(i543) = -6.25$
	$\varphi(j521) = -22.98$
$\varphi(k654) = 127.07$	$\varphi(k612) = 161.36$

As a result, the vertical detachment of an electron is energetically more probable from the cyclic isomer than from the chain-like isomer. All the anions larger than the dimer are stable against dissociation into the individual molecules and a free electron, and here the cyclic isomers are even more stable (see Table 5).

To conclude, the calculation of the cyclic and chain-like water pentamer and hexamer anions at the unrestricted Hartree—Fock level with the 4-31++G and 4-31++G** basis sets showed the following. The formation of chain-like anions requires less energy, and the structures formed are fairly similar to the original neutral structures. The excess electron density is localized chiefly on the H nuclei of that terminal water molecule that acts as an acceptor of the H-bond proton. The attachment of an electron to a cyclic oligomer requires substantially more energy and results in more noticeable restructurization. In the final, more compact structure, the excess electron density is typically localized near the H nuclei that are most distant in the neutral structure and that substantially approach each other after the attachment of an electron. Both cyclic and chain-like pentamer and hexamer anions are stable against dissociation into the constituting water molecules and a free electron. The vertical detachment of an electron from the pentamer anions and from the cyclic hexamer anion proceeds with the liberation of energy. However, in the case of the chain-like hexamer anion, the detachment

Table 5. Energetic characteristics (eV) of the $(H_2O)_n$ oligomers and their $(H_2O)_n^-$ anions (n = 5, 6)

n	$-EA_{vert}$		$-EA_{ad}$		$-VDE$		S	
	I	II	I	II	I	II	I	II
5 (chain-like)	0.237	0.306	0.075	0.186	0.042	0.130	1.167	0.756
5 (cyclic)	0.967	0.923	0.879	0.641	0.489	0.551	1.044	0.752
6 (chain-like)	0.195	0.266	0.025	0.136	−0.032	0.059	1.570	1.099
6 (cyclic)	0.954	0.905	0.723	0.463	0.350	0.427	1.608	1.248

Note. I, 4-31++G; II, "4-31++G**".

energy is close to zero, which agrees with the experimental data and indicates metastability of the anion.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32343a).

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Received June 17, 1996