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Small Charged Water Clusters: Anions

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Water cluster anions $(H_2O)_n^-$ with $n = 2-8$ are considered as a gradual approach to the model of a hydrated electron. In the structures of cluster anions optimized at the unrestricted Hartree−Fock level, the excess electron density is always localized around protons of the hydrogen atoms uninvolved in hydrogen bonds. Yet, two types of structures are distinguished. In the first type, the excess electron is localized in an individual though deformed cluster. The second type embraces the face-to-face anionic species, in which two confronted clusters that are not joined via a usual hydrogen bond localize the electron. The vertical energies of the electron detachment from the anions estimated in the second order of the Møller−Plesset perturbation theory are positive already for the trimer anion consisting of the confronted monomer and dimer. A transformation of the plain chainlike neutral octamer into the most stable face-to-face anion upon adding an electron shows that eight molecules already can form a stable solvation shell of the excess electron. Varying the exponent of the diffuse s functions centered on hydrogen nuclei showed that there is probably an optimum exponent of about 0.020 for the description of the hydrated electron. Two types of excess electron localization are distinguished, namely, surface and interface.

Introduction

As was shown in ref 1, an energy of about 9.0−9.5 eV is sufficient for the positive ionization of small water clusters. The relaxation and structure reorganization of clusters that had lost an electron were considered in ref 1. Now, we proceed to the localization of the electron knocked out from the original neutral cluster. Obviously, the electron should be captured by neighbor water molecules and, thus, solvated. The consideration of the hydrated electron can be started with the modeling of small water cluster anions.

$(H_2O)_n^-$ anions are formed as a result of the interaction between the supersonic molecular expansion of water clusters and free or quasifree electrons.[2−6] The kinetic energy of electrons typically does not exceed 2 eV and approaches zero under special conditions. Long-living water anions are formed due to the electron attachment to the preformed neutral clusters. Such structures involve 11 or more molecules. The smaller anions seemingly have the free energy that exceeds the vertical energy of electron detachment (VDE) and, therefore, almost immediately lose an electron. The structures can be stabilized in a rare-gas flow that contains no more than 1% water molecules and clusters. In the collisions with the newly formed small water anions, the rare-gas atoms take off their excessive energy. As a result the amount of small water anions increases. In pure water expansions, a similar stabilization may be reached due to the attachment of additional water molecules, which increases the size of anionic species detected.

Judging from the data of ref 7, the anions smaller than a hexamer should be metastable: the experimental vertical energies of detachment of an electron from the cluster anions $(H_2O)_n^-$ with $n = 11-69$ were fitted to the straight line VDE($n^{-1/3}$), which intersects the abscissa axis around $n = 5-6$. This means that water anions with $n < 11$ can exist (though some as probably metastable species) and, as such, can be considered as the first tentative model of the hydrated electron.

Theoretical models that are commonly used are either a set of water molecules that possess a negative charge and are arranged around a cavity with the diffuse s or p functions placed in the center of the cavity,[8−11] or $(H_2O)_n^-$ clusters with a large set of diffuse functions centered between nuclei.[12−14] In any case, the structure of the anion is often presumed, and the atomic basis set is augmented with a large number of diffuse functions, and the result strongly depends on the amount, type, and location of these functions.

The extra diffuse functions do provide additional possibilities for describing the excess electron, but they can distort results, and the larger their number, the more probable the artifacts. The problem may also be in the type and quality of the functions used. The Gauss functions which people use are no more than an approximation of the one-center eigenfunctions; the exponents of the functions are optimized with regard to certain electronic configurations. For example, the conventional N-31G and N-311G basis sets and the Pople exponents of diffuse and polarization functions are good enough for the description of typical species. In the case of such complex structures as the hydrated electron, the conventional approximation is probably not so fit for the purpose.

Therefore, we used no diffuse functions centered between nuclei, but varied the exponents of the standard atomic orbitals. The basis set was the same as that we found[1] sufficient for an adequate description of neutral and positively charged clusters, namely, 4-31G supplemented with diffuse and polarization functions on all nuclei. Four different exponents of the diffuse s function centered on protons were considered: the standard Pople $\alpha = 0.036$ and three smaller values of 0.024, 0.017, and 0.006.

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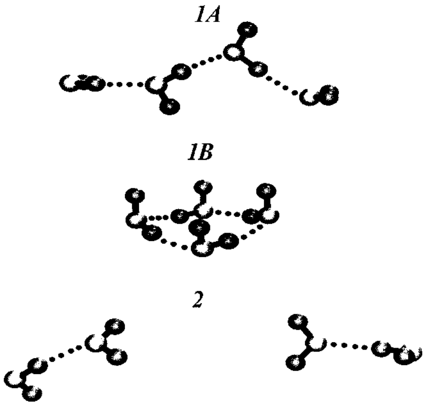

Figure 1. Structures of the water tetramer anion of types 1A, 1B, and 2.

We varied the exponents of the s(H) diffuse functions only, because our previous tentative results[15] showed that precisely these functions of one or several water molecules predominantly contribute to the highest occupied molecular orbital (HOMO). The contributions from the s and p functions centered on O nuclei are substantially smaller.

This result agrees with the experimental and theoretical data. The angular distribution of photoelectrons emitted from the $(H_2O)_{18}^-$ cluster indicates the probable s character of the excess electron orbital.[16] In terms of a theoretical model, which combines the quantum mechanical treatment of the electron with the classical description of the solvent, the ground state of the hydrated electron is well described with a localized s function.[17] Note that the theoretical electron hydration energy is 3.2 eV in close agreement with the experimental estimate of 3.3 eV.[7]

Calculation Technique

The geometry optimization of water anions $(H_2O)_n^-$ with $n = 2-8$ was carried out at the unrestricted Hartree−Fock level with the 4-31++G** basis set. No restriction was imposed on the mutual arrangement of molecules or their geometry. Then, the electron correlation energy was taken into account in the second order of the Møller−Plesset perturbation theory (MP2). All the structures considered below correspond to the minima on the potential energy surfaces of anions, which was confirmed by the vibrational analysis. As the initial approximation in the optimization run, the optimal configuration of the corresponding neutral cluster was usually (but not always) taken. We considered cyclic, cagelike, and chainlike configurations of neutral clusters.

The possibility of the existence of anions was judged from the vertical energy of the detachment of an electron from the anion taken in its optimal configuration (VDE):

$$\mathrm{VDE} = E((H_2O)_n) - E((H_2O)_n^{\ -})$$

where $E((H_2O)_n^-)$ and $E((H_2O)_n)$ are the energies of $(H_2O)_n^-$ and $(H_2O)_n$ clusters taken at the same optimized configuration of the anion.

Structures and Stability of Cluster Anions

Two dominating types of water anions can be distinguished according to the peculiarities of geometry and hence the character of the excess electron density localization. Typical configurations of both types are shown in Figure 1. In one case, the excess electron is localized in a single neutral cluster, and two kinds of such anions were found, namely, (A) predominantly chainlike clusters, in which the excess electron density is localized on a molecule that acts as a proton acceptor in the hydrogen bonds, and (B) cyclic and relatively compact structures with the excess density localized around nuclei of four free hydrogen atoms H_{fr} (uninvolved in hydrogen bonds). The structures of the second type represent a situation when two non-H-bonded species participate in the localization of the excess electron. These are composed of two confronted chains with the excess density localized around four hydrogen nuclei of those two molecules which directly face each other.

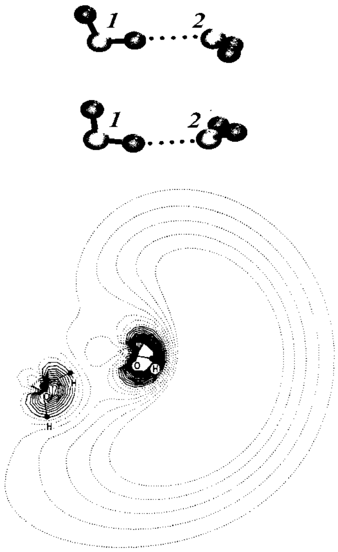

Figure 2. Optimized configurations of the neutral (upper) and negatively charged (lower) water dimer and the contour plot of the HOMO of the anion.

In the expansion of HOMO, the diffuse s functions centered on hydrogen nuclei dominate, and typically the number of these nuclei tends to four, provided that the original structure allows such a transformation.

Structures of the First A Type. The dimer anion and neutral dimer have different configurations (Figure 2). Upon adding an electron, molecule 2, which is an acceptor of the H-bond proton, rotates so that its hydrogen nuclei appear on the same side of the O···O line as the free H atom of molecule 1. The HOMO involves with comparable weights the diffuse atomic orbitals (AOs) of all hydrogen atoms and the O atom of molecule 2, and its contour plot is shown in Figure 2. These results are very similar to those of ref 13, where a high-quality basis set for the dimer was supplemented with a set of 7s and 7p functions with the exponents to 0.000 001 specially for the description of the excess electron. This fact shows that our approach is reasonable and there is no need to use extra diffuse functions centered between nuclei. The possible negative VDE values we may obtain mean no more than that the corresponding anion is stable only in certain surroundings, such as the cage of argon atoms. Decreasing the exponents of the diffuse functions, we simply allow the electron to move as far from the cluster as it can or “wants” and will finally obtain a zero vertical detachment energy.[18]

The chainlike structures of different sizes are very similar (Figure 3): each subsequent member of the series can be obtained by simply adding a water molecule to that end of the chain which least noticeably contributes to the localization of the excess electron density. Upon capturing an electron, the chains of molecules contract and become more voluminous: the O−H distances slightly increase, while the O···H distances and O−H···O angles decrease. Two chainlike configurations of the

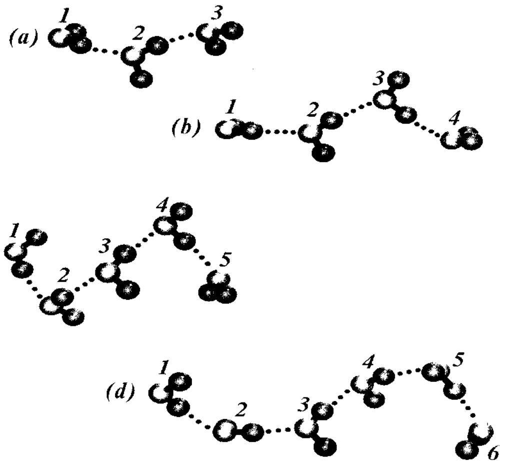

Figure 3. Optimized chainlike configurations of the anions of type 1A: (a) trimer; (b) tetramer **I**; (c) pentamer **II**; and (d) hexamer **I**.

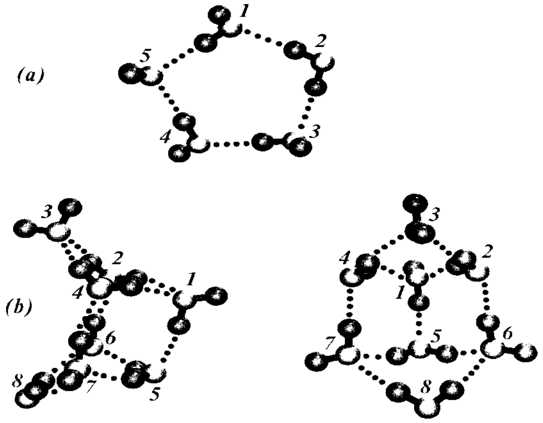

Figure 4. Optimized cyclic configurations of type 1A: (a) pentamer **III**; and (b) octamer **I** shown in two projections.

pentamer anion have much in common, though isomer **I** resembles a contracted helical spring, while isomer **II** looks like a weakened and bent spring (only isomer **I** is shown in Figure 3).

In all of the chainlike anions, the diffuse s orbitals centered on the nuclei of the terminal molecule dominate in the expansion of HOMO. This is illustrated by the results of Löwdin population analysis:

anion	dimer	trimer	tetramer **I**	pentamer **I**	pentamer **II**	hexamer **I**
molecule k	2	3	4	5	5	6
$q(k)$, au	−0.89	−0.83	−0.79	−0.66	−0.64	−0.60

A similar character of the excess electron localization can be observed in cyclic structures as well. These are isomer **III** of the pentamer anion and isomer **I** of the octamer anion (Figure 4). These isomers are stabilized by the largest number of hydrogen bonds and, therefore, have the lowest energy among the structures of the same size. The predecessor of octamer anion **I** was the neutral cubic octamer. Upon capturing an electron, the cube opens at one vertex, and two of six cube faces become substantially deformed. Nevertheless, the structure preserves a high symmetry. In both anions, the excess electron is localized around two hydrogen nuclei of one molecule (in pentamer **III**, $q(5) = -0.75$ au, and in octamer **I**, $q(3) = -0.84$ au), and the HOMOs have essentially the same character as the HOMOs of the chainlike isomers.

The latter fact is worth specially noting. As is shown below, the HOMO tends to span four free hydrogen nuclei. This is not the point in the cubic octamer. The excess electron is not localized around free hydrogen nuclei that point outside the cube and the distances between which are about 5.63 Å. The only explanation we can suggest is that the quoted internuclear distances are larger than those necessary for an efficient overlapping of the corresponding diffuse orbitals. We will turn to this point during discussion of the second type of structures.

TABLE 1: VDE Estimates (eV) for the Anions Depending on the s(H) Exponent α[a]

anion	VDE α(s) = 0.036	VDE α(s) = 0.024	VDE α(s) = 0.017
First Type A Chainlike Configurations			
dimer	−0.56	−0.37	−0.24
trimer	−0.33	−0.17	−0.06
tetramer **I**	−0.19	−0.05	0.04
pentamer **I**	0.06	0.06	0.13
pentamer **II**	0.08	0.08	0.13
hexamer **I**	0.20	0.18	0.18
Cyclic Configurations			
pentamer **III**	0.11	0.23	0.28
octamer **I**	−0.15	−0.01	0.07
First Type B			
tetramer **II**	−0.26	−0.21	−0.17
pentamer **IV**	−0.23	−0.18	−0.15
hexamer **II**	−0.15	−0.16	−
hexamer **III**	−0.08	−0.08	−0.06
Second Type			
dimer	−0.34	−0.22	−0.15
trimer **1&2**	−0.03	0.02	0.06
tetramer **2&2**	0.25	0.26	0.26
hexamer **3&3**	0.57	0.53	0.50
hexamer **2&4**	0.53	0.50	0.46
octamer **4&4**	0.77	0.62	0.62
octamer **2&6**	0.72	0.68	0.65

[a] We failed to find an isomer of cyclic hexamer anion **II** without an additional hydrogen bond, when the s(H) exponent was 0.017.

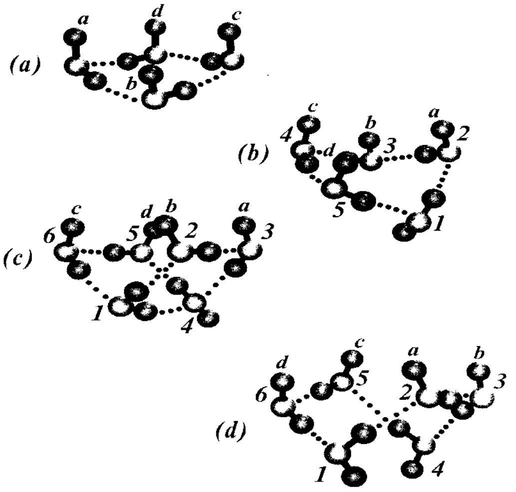

Figure 5. Optimized configurations of the anions of type 1B: (a) tetramer **II**; (b) pentamer **IV**; (c) hexamer **II**; (d) hexamer **III**.

The vertical energies of electron detachment from the considered anions of the first type are listed in Table 1. An increase in the diffuseness of the s orbitals centered on hydrogen nuclei results in the stabilization of the anions. Even the tetramer anion should keep an excess electron. Furthermore, with the conventional exponent, already the pentamer anion is predicted to be stable, in general accord with the experimental work.[7]

Structures of the First B Type. In these cyclic and compact configurations (Figure 5), four free hydrogen atoms form a slightly distorted square. The diffuse s functions centered on these nuclei provide the largest contributions to the HOMO.

The neutral cyclic tetramer has an almost S_4 symmetry: two free H atoms are on one side of the plane of oxygen atoms; the remaining two are on the other side. In the anion **II**, all free hydrogen atoms are on the same side of the plane of oxygen atoms, and the whole structure has a slightly distorted C_4 symmetry.

In the anion of cyclic pentamer **IV**, molecules 2, 4, and 5, the most distant in the original neutral isomer (which is envelope-shaped), approach each other. Accordingly, the diffuse functions of the free hydrogen atoms of these molecules and molecule 3 provide the largest contributions to the HOMO.

The most stable isomer of the neutral hexamer has a book-shaped configuration resembling a prism. On transforming into the anion, the dihedral angle between the two plains decreases by half, and the whole structure becomes more symmetric. Molecules 2, 3, 5, and 6 form a slightly twisted quadrangle, in which the mutual arrangement and the orientation of the $O-H_{fr}$ bonds are similar to those of the tetramer **II** anion. Two such isomers of the hexamer anion (**II** and **III**) differ only in the existence of an H-bond between molecules 1 and 4 that negligibly contributes to the localization of the excess electron density. The diffuse functions of the remaining free hydrogen nuclei dominate in the expansion of the HOMO, which is illustrated by the corresponding atomic charges:

anion	tetramer **II**	pentamer **IV**	hexamer **II**	hexamer **III**
q(a) = q(c), au	0.01	−0.01	−0.01	0.02
q(b) = q(d), au	0.12	0.15	0.15	0.13

These anions are unstable against the detachment of the excess electron, as can be judged from the data listed in Table 1. This may be explained as follows. The distances between the hydrogen nuclei, the diffuse functions of which dominate in the expansion of HOMO, are about 3.53 Å in the tetramer anion, 3.54 and 3.73 Å in the pentamer anion, and 3.59 and 4.45 Å in the hexamer anion. (The internuclear distances in text were calculated for the anioinic structures optimized with the s(H)-function exponent of 0.017.) These distances result from a compromise between the optimum distances between the H-bonded molecules arranged in a cycle and the optimum distances between the maxima of the radial electron densities of the diffuse s(H) functions. Probably, such distances are improper for the construction of a "good" orbital of the excess electron. This point is considered in detail for the second type of structures, to which we proceed now.

Structures of the Second Type. In most cases, these structures were artificially constructed rather than obtained by a direct optimization of the anionic species with the initial configuration of the optimal neutral cluster. However, this is not the point in the case of the octamer. We failed to find a plain chainlike configuration of the octamer anion of the first type. Instead, as a result of the addition of an electron to the original chain of the neutral octamer, a hydrogen bond between two molecules of the octamer was broken, the molecules reorient "around" the excess electron, and, finally, the electron localizes between two chains, consisting of two and six water molecules, respectively. The structure is additionally stabilized by newly formed hydrogen bonds. This means that eight molecules are already able to solvate an excess electron in strict agreement with the conventional concept of the process of solvation: some original bonds between solvent molecules are broken, and some other bonds are formed.

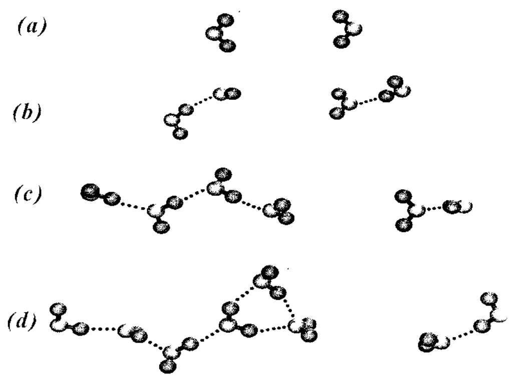

Figure 6. Optimized face-to-face configurations of cluster anions: (a) dimer **1&1**; (b) tetramer **2&2**; (c) hexamer **2&4**; (d) octamer **2&6**.

In the face-to-face structures (Figure 6), the dihedral angle between the planes of two molecules that directly face each other varies from 0° to 90°. It is the smallest in the dimer—the only face-to-face anion that, according to our estimates, does not bind the excess electron. In the remaining structures, the angle is close to 90°. Taking into account that the distances between the hydrogen atoms of the two molecules are almost equal (differ by no more than 5−8%), we can say that these H atoms lie in the vertexes of a stretched tetrahedron. The corresponding H···H distances are as follows (see Figure 6) (the specifications of the anions such as ***i&j*** mean that the faced chains consist of ***i*** and ***j*** molecules, respectively): 5.38−5.53 Å in tetramer **2&2**; 5.18−5.43 Å in hexamer **2&4**; 5.10−5.31 Å in hexamer **3&3**; 4.97−5.43 Å in octamer **2&6**; 4.95−5.27 Å in octamer **4&4**. Thus, the average H···H distance contracts as either one or both constituting chains lengthen.

If we recall now the H···H distances between the free hydrogen nuclei of the neutral cubic octamer (5.63 Å), we will see that they are larger than even the largest H···H distance in the face-to-face tetramer anion. This fact may explain why, in the case of the cubic octamer, the HOMO did not span the whole cluster, but mainly one molecule (at the opened vertex) and those next to it.

Turn back to the face-to-face anions. As the length of chains increases, the HOMO spans more molecules of the chains and acquires a pronounced bonding character. This means that the excess electron has no tendency to detach from the structure (as is illustrated by the corresponding VDE values), but does bind and keep the two chains of water molecules together (Table 1). Especially interesting in this respect is that, in the case of the stable hexamer and octamer face-to-face anions, the VDE value increases as the diffuse s(H) orbitals become *less diffuse*.

As to the absolute energies of the anions (estimated at the MP2/4-31++G** level), starting with the tetramer, a slight minimum is observed at α of 0.024−0.017:

	$\alpha = 0.036$	$\alpha = 0.024$	$\alpha = 0.017$	$\alpha = 0.006$
dimer	−152.316 42	−152.320 59	−152.323 10	−152.336 92
trimer **2&1**	−228.500 06	−228.502 93	−228.504 65	−228.505 46
tetramer **2&2**	−304.682 57	−304.684 50	−304.685 04	−304.682 21
hexamer **2&4**	−457.044 57	−457.045 90	−457.045 43	−457.041 34
octamer **2&6**	−609.406 74	−609.407 10	−609.406 34	−609.400 85

This may also be considered as an indication that there is an optimum exponent of the s(H) function for the description of the excess electron, and it is about 0.020. It is worth noting that it should not be as small as 0.000 001 or even 0.001. Furthermore, the stability and the bonding character of the HOMO become more pronounced as the number of molecules exceeds three in at least one of the two confronted chains (hexamer **2&4** and octamer **2&6**). This result correlates in some way with the early conclusions of refs 9−11 that there should be more than two or three coordination shells of water molecules around an electron for its effective binding.

Furthermore, if we plot the VDE values of the face-to-face anions with $n \geq 3$ (in our calculations, $(H_2O)_3^-$ is the smallest cluster that has a positive VDE) estimated with the s(H) exponent $\alpha = 0.024$ (a value close to that we suppose to be optimal), we get a straight line:

$$-\text{VDE} = -2.29 + 3.25\ (1/n^{1/3})$$

Similar linear approximations but with different slopes can be obtained for the VDE estimates with the basis sets involving the s(H) exponents of 0.036, 0.017, and 0.006 as well. All slopes lie in the range from 2.95 to 3.95 eV/$n^{-1/3}$, which is intermediate between the experimental estimates of 0.52 and 1.37 eV/$n^{-1/3}$ for the anions of the same and comparable size[19] and 5.73 eV/$n^{-1/3}$ for the anions with $n = 11-69$.[7] Note also that the VDEs of $(H_2O)_6^-$ (with $\alpha = 0.024$) (the VDE estimates with different α values are very close to each other, and despite the fact that the VDE obtained with $\alpha = 0.017$ or 0.006 may be even closer to the experimental data, we consider $\alpha = 0.024$ as probably providing the optimum description of anions) are in good agreement with the experimental data,[19] namely, (i) 0.18 eV for the first A type anion and 0.21 eV for isomer **I** in ref 19 and (ii) an average of 0.51 eV for the face-to-face anions and 0.48 eV for isomer **II** in ref 19. The idea of refs 19 and 20 that isomer **I** has a more diffuse excess electron distribution as compared to isomer **II** also correlates with our data: the electron localization between two confronted chains of molecules is more "compact" as compared to the localization around one terminal molecule. Moreover, the data of ref 7 are also in accord with our estimates. The VDE of the less and the more stable isomers are about 0.20 and 0.45 eV, respectively (both values are roughly estimated from the corresponding plot in ref 7).

Unfortunately, there are no similar data on octamer isomers in ref 19, and therefore, we cannot compare experimental and our nonempirical data for $n = 8$, which would either confirm or disprove a conclusion that the face-to-face structures of anions are also observed in the experiment. In the case of smaller anions, such a comparison is meaningless, since the second type of anions of this size can scarcely be formed under particular experimental conditions.

Of course, the coincidence of the VDE values may be accidental, but the linear shape of the VDE($n^{-1/3}$) dependence confirms that our model approach is essentially correct, and only some qualitative changes may be introduced in the picture of anions on going to the higher levels of theory (such as CISD).

There is one more aspect. Two types of electron localization are supposed to exist, namely, *surface* and *internal*.[21] Path-integral molecular dynamics simulations with a specially constructed pseudopotential of the electron−water molecule interaction forced the authors of ref 21 to conclude that internal localization of the excess electron becomes energetically favored at $n \approx 64$. Later, on the basis of photoelectron spectroscopy data for the anions $(H_2O)_n^-$ with n up to 69, the authors of ref 7 have put forward a supposition that a transition from the surface to internal localization of an electron should take place at $n = 11$ or even 6. In our first type of anions, the excess electron density is localized around the nuclei located outside an H-bonded cluster of water molecules, and the character of the localization can be named *surface* in conventional meaning of the term. The anions of the second type represent principally another type of localization, which, nevertheless, can scarcely be named internal. In fact, when a second-type anion loses an electron, it is no longer a unit: two unbonded water clusters of smaller size are practically independent. This means that it is an electron which binds two clusters that face each other, and the character of localization should more properly be named *interface*. Our VDE estimates show that this interface localization may be realized already in the trimer and is efficient in the anions starting from the hexamer.

Conclusions

Two main problems concerning water cluster anions gained the most attention: the smallest stable cluster and the character of the excess electron localization. Our data on $(H_2O)_n^-$ clusters with $n \leq 8$ provide tentative answers to both questions.

The excess density is always localized around free hydrogen nuclei of either one or several molecules. Nevertheless, two types of anionic structures are distinguished. The anions of the first type are either chainlike or compact cyclic and can be formed when the excess electron is captured by a lone relatively small neutral cluster. The second type of anions arise either if the electron is localized between the confronted ends of two chains that are not mutually hydrogen bonded, or when the electron is captured by a medium-sized cluster, e.g., chainlike, which restructures to form a similar face-to-face anion.

Already the trimer composed of the confronted dimer and monomer has a positive vertical energy of electron detachment. Starting from the pentamer, the anions of the first A and second types are stable against detachment of the excess electron.

In the first type of structures, the localization can be named surface, while the second type of structures manifest the interface electron localization. The most stable (as regards the electron detachment) are those structures in which the expansion of HOMO involves with the highest weights the diffuse s orbitals of four free hydrogen nuclei that lie in the vertexes of a stretched tetrahedron. In this case, the HOMO has a pronounced bonding character.

A comparative analysis of the s(H) functions with various exponents shows that there is probably an optimum α value of about 0.020, which provides the minimum energy of the most stable anionic structures (face-to-face configurations).

Now to our final comment: It is evident that the detachment of an electron localized by (or between) two confronted chainlike clusters makes the chains unbonded. Hence, it is only a matter of the personal taste and views of whether the process in question be named the desolvation of an electron or the breakage of an electron bond between two water clusters.

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