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A Study of Structural and Dynamic Characteristics of Water Clusters of Na+, K+ and Cs+ ions

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Received May 24, 1994

Abstract – The clusters consisting of Na+, K+, and Cs+ ions surrounded by 63 water molecules are studied by molecular dynamics. Structural and dynamic characteristics of these clusters are calculated. A mechanism of water molecule exchange near metal ions is investigated. The results of this study are compared with previous data obtained by the same group for ion clusters containing 24 water molecules. An increase in the water molecule mobility in the K+- and Cs+-based clusters is explained by the formation of a large amount of interacting hydrogen bonds in these clusters.

Water clusters of Na+, K+, and Cs+ were extensively studied by molecular dynamics [1 - 7]. The important role of the ions indicated in natural and technological processes and the possibility of employing the ionic water clusters as model systems stimulated this study. Different aspects were studied in the papers enumerated above: for example, the dependence of different cluster properties on the potential energy characteristics, multiparticle effects, the local electric field in the vicinity of an ion, the most plausible configurations of a water molecules in the hydrate shells, and others. Earlier, we studied the ion clusters of Na+, K+, and Cs+ with 24 water molecules [5 - 7]. We were especially interested in the structural and dynamic characteristics of these clusters. We have shown that the mechanisms of water molecule exchange near the Na+ and K+ ions differ: the process is single-particle for the Na+ cluster and multiparticle, i.e., cooperative, for K+. The Cs+-based cluster with 24 water molecules is too small to make any definite conclusions about its exchange mechanism: the second coordination sphere of the Cs+ ion in this cluster is not completely filled. The water molecule exchange near the K+ ion was accounted for by a significant fraction of bifurcating hydrogen bonds in the first hydrate sphere of this ion, which were considered as defects of the H-bond network [6].

The objective of this work is to study the changes in the structural and dynamic characteristics of ion (Na+, K+, and Cs+) clusters by increasing the number of water molecules in these clusters to 63. We understand that in order to simulate the real situation in water solution, a substantially larger number of water molecules must be taken into account. We consider this work as a certain step toward the simulation of a transition from small water clusters to water solution.

The molecular dynamics method was chosen as the main investigational tool: this allows us to determine not only structural and energetic characteristics but dynamic parameters as well. The calculations of the ion cluster characteristics were based on the computer code worked out by Tytik [8]. In this code, the algorithm, developed by Grivtsov [9], allows an increase of the integration step ten times in comparison with conventional procedures; the accuracy is more than acceptable. This algorithm is very sensitive to the initial configuration; therefore, the model cluster, consisting of 63 water molecules with an ion in the center, was calculated by the Monte-Carlo method using the Metropolis approach [10] up to its reaching thermodynamic equilibrium. To reduce the calculation time, the modeled cluster was "cooled" and "heated" several times. The cluster temperature was empirically chosen as 290 K. The integration step was 2×10^{-15} s. Calculated data were displayed in every 5000 steps after the thermodynamic equilibrium was attained. We performed 40 000 - 50 000 steps, that is about 10^{-10} s in real cluster time. For each system, no less than five calculations were performed. The calculations were carried out at the Institute of Physical Chemistry of Russian Academy of Sciences and at Computer Center of Dortmund University (Germany).

To simulate a water–water interaction, the atom–atom Poltev–Malenkov potential [11] was used, that is, a three-point model of water molecule with the force centers located on the atoms. An ion–water interaction potential was chosen stet to be consistent with quantum-chemical calculations of Clementi's group [12], with distances in crystal hydrates [13, 14], and with the coordination numbers of the ions considered in gas phase [15].

Table 1. The parameters of interaction potentials

Interaction	A	B	n
O–O	410 000	3700	12
H–H	3600	3760	12
O–H	3800	40	10
Na⁺–O	235 000	1500	12
K⁺–O	1 391 000	3680	12
Cs⁺–O	2 500 000	1035	12

Table 2. The energetic characteristics of interaction in the water clusters M⁺–24H₂O and M⁺–63H₂O

Cluster	$-E_{i-w}$	$-E_{w-w}$	$-E_{tot}$
Na⁺–24H₂O	151	102	253
Na⁺–63H₂O	230	353	583
K⁺–24H₂O	127	119	246
K⁺–63H₂O	181	405	586
Cs⁺–24H₂O	74	129	203
Cs⁺–63H₂O	92	426	518

Note: E_{tot} is the total energy of the cluster considered; E_{i-w} and E_{w-w} are the ion–water and water–water interaction energies, respectively.

The potential was represented as follows

$$U_{ij} = \frac{A_{ij}}{r_{ij}^n} - \frac{B_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}}. \qquad (1)$$

The potential parameters are presented in Table 1.

RESULTS AND DISCUSSION

The clusters of Na⁺, K⁺ and Cs⁺ with 63 water molecules were studied. The crystallographic radii of these ions are different [16]: r(Na⁺) = 0.96 Å, r(K⁺) = 1.33 Å,

r(Cr⁺) = 1.65 Å; the covalence degrees in the interaction with water were 10 and 3% for Na⁺ and Cs⁺ ions, respectively [17, 18]. We presented these characteristics of the ions considered because, in accordance with the Frenkel concept of thermal movement in liquids, short-range forces play a key role in exchange processes and, therefore, an activation energy depends not on the total interaction energy of particles, but on its variation at small distances [19, 20]. For this reason, it is very important to know the relative contribution of noncoulombic forces in the ion–water interaction because they exhibit a much stronger dependence on the distance between particles as compared to the coulombic forces. Table 2 shows the energetic characteristics for the ion clusters of Na⁺, K⁺, and Cs⁺ with 24 and 63 water molecules. We found that, in passing from the Na⁺ to Cs⁺, the ion–water interaction energy in clusters decreases while water–water interaction increases.

The structure characteristics of 24- and 63-water-molecule clusters of the ions studied are listed in Table 3. Before inspecting this table, it is worthwhile to turn to Fig. 1 where the radial distributions (RD) for ion–oxygen distances in the 63-water-molecule clusters are presented. The data for the Cs⁺ ion are presented in a separate figure because the quantitative changes with the increasing of the water content were revealed only in the case of this ion; the complicated second maximum in the ion–oxygen RD for clusters with 24 water molecules is split into two pronounced maxima, indicating that in the cluster with 63 water molecules, three distinct hydrate spheres are formed. The locations of the second and third maxima on RD for ion–oxygen in the Cs⁺–63H₂O cluster are consistent with RD for pure water. Note that, within 40×10^{-12} s after the calculations are started, the Cs⁺ ion migrates to the cluster boundary   . as though the cluster extrudes from itself a large particle with a single charge. In the case of the Cs⁺–63H₂O cluster, the resistanse of the

Table 3. The structure characteristics of water clusters of the Na⁺, K⁺, and Cs⁺ ions

| Parameter	24H₂O			63H₂O		
	Na⁺	K⁺	Cs⁺	Na⁺	K⁺	Cs⁺
Mean coordination number	7.2	8.8	9.0	7.5	9.5	10.6
Location of the first maximum in the ion–oxygen RD (Å)	2.40	2.85	3.20	2.40	2.85	3.25
Location of the second maximum in the ion–oxygen RD (Å)	4.45	4.55	5.65	4.55	4.65	4.80
Distance between the first and second maxima in the ion–oxygen RD (Å)	2.05	1.70	2.45	2.15	1.80	1.55
Location of the first minimum in the ion–oxygen RD (Å)	3.25	3.50	4.15	3.15	3.50	4.00
Ordinate of the first minimum in the ion–oxygen RD (arb. units)				0.5	1.0	1.7
Location of the first maximum in the ion–hydrogen RD (Å)	3.05	3.40	3.60	3.00	3.40	3.70
Location of the second maximum in the ion–hydrogen RD (Å)	5.10	5.30	5.7⁵	5.10	5.30	5.35
Distance between the first maxima of the ion–hydrogen and ion–oxygen RDs (Å)	0.65	0.55	0.40	0.60	0.55	0.45
Distance between the second maxima of the ion–hydrogen and ion–oxygen RDs (Å)	0.65	0.75	0.10	0.55	0.55	0.55
Location of the first maximum of the oxygen–oxygen RD (Å)	2.75	2.70	2.71	2.72	2.71	2.71
Location of the second maximum of the oxygen–oxygen RD (Å)	4.75	5.00	4.46	4.70	4.30	4.30
Distance between the first and second maxima in the oxygen–oxygen RD (Å)	1.95	2.25	1.75	1.98	1.59	1.59
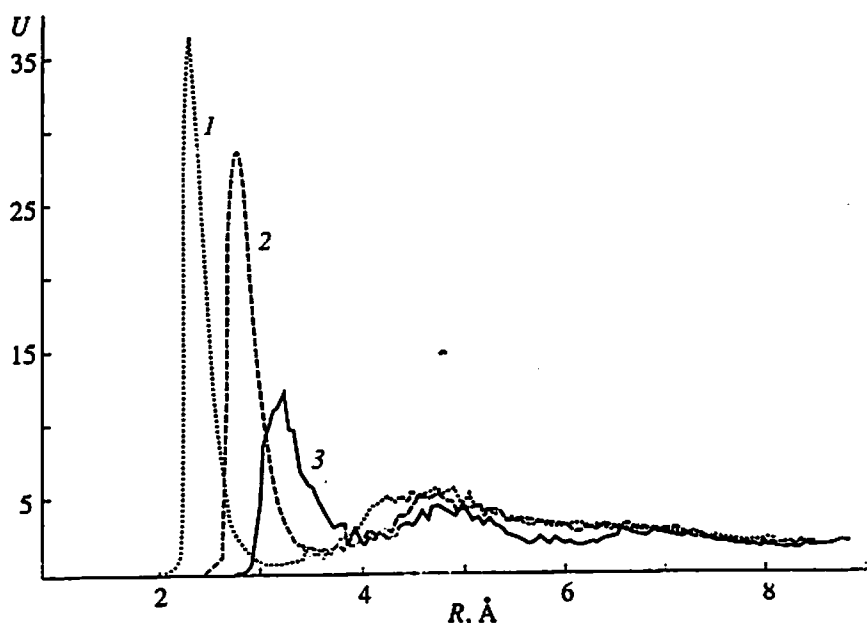
Fig. 1. Radial distribution function for ion–oxygen distance in the ion–63H$_2$O clusters: (1) Na$^+$, (2) K$^+$, (3) Cs$^+$.
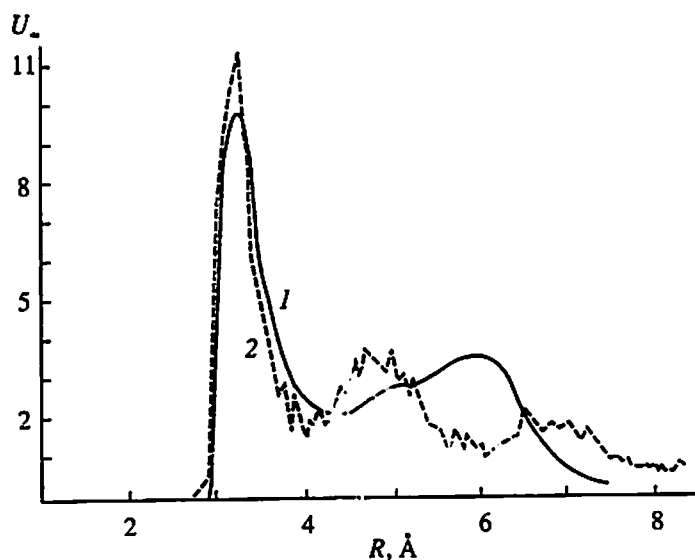

Fig. 2. Radial distribution function for ion–oxygen distance in the Cs$^+$ clusters with (1) 24 and (2) 63 water molecules.

two forces of ion–dipole interaction and elasticity of the H-bond network in water [21] is clearly exhibited.

Considering Table 3 and focusing on the changes in the cluster structure characteristics with water content, one can note an increase in the coordination number of ions, which is highest for Cs$^+$. Position of the first maximum in RD of ion–oxygen is virtually invariant for large water clusters of all three ions. The location of the second maximum is shifted to higher r values for the Na$^+$ and K$^+$ clusters and to lower r values for Cs$^+$. The distance between the first and second maxima in RD of ion–oxygen is slightly increased in the Na$^+$ and K$^+$ clusters and, visa versa, decreased for Cs$^+$. The location of the first minimum for all the clusters considered

is, in fact, invariable; the depth of the minimum slightly decreases for the Na$^+$ and K$^+$ clusters and increases for the Cs$^+$ cluster when passing to clusters with a higher content of water molecules.

The comparison between RD of ion–oxygen and ion–hydrogen yields information on the orientation of the water molecules in the first and second hydrate spheres of ions and also in an intermediate region. Note that the smallest distance between the above-mentioned maxima is in the Cs$^+$ cluster and it increases with the content of water molecules in clusters.

The RD for oxygen–oxygen and oxygen–hydrogen in the clusters considered allows us to conclude that the angle between hydrogen bonds in hydrate spheres of
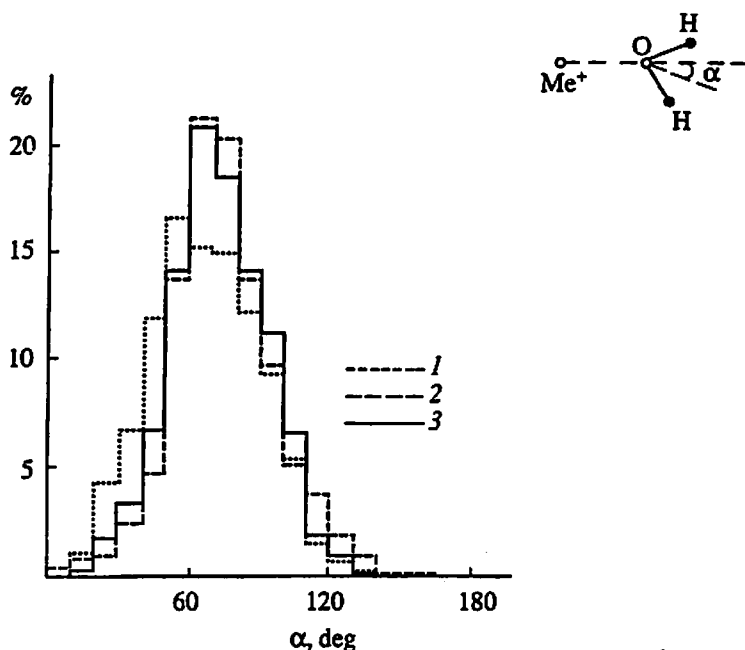
Fig. 3. The distribution of water molecules over the angle α (formed by the dipole moment of a water molecule and the direction to ion) in the intermediate region (the first minimum in the ion–oxygen RD) for the 63-water-molecule clusters: (*1*) Na⁺, (*2*) K⁺, (*3*) Cs⁺.
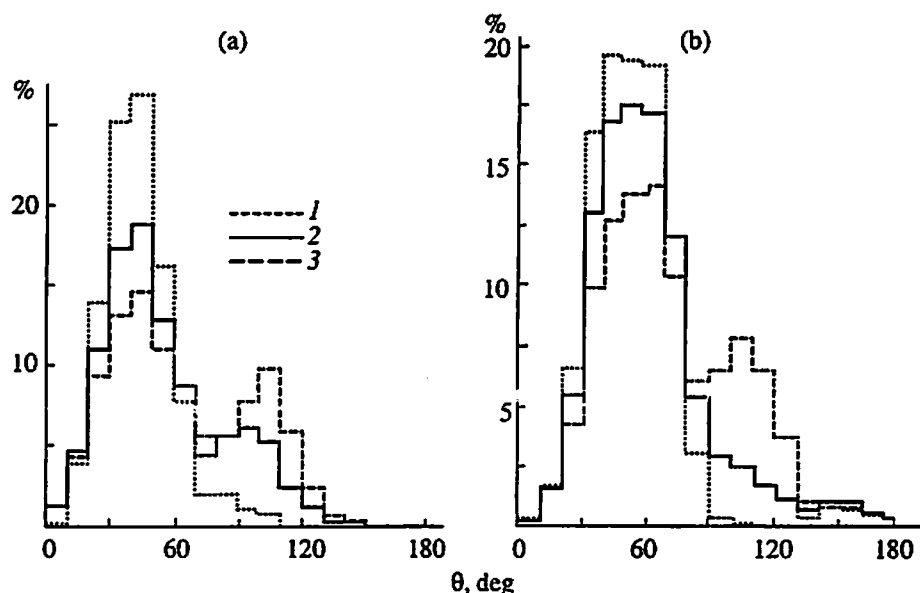

Fig. 4. Distribution of water molecules over the angles of hydrogen bonds (a) in the first hydrate sphere and (b) in the intermediate region for the Cs⁺–63-water-molecules clusters for different criteria of hydrogen bond formation: $r(O-O)$ = (*1*) 2.9; (2) 3.2; (*3*) 3.5 Å.

water clusters changes. For clusters with a higher water molecule content, the distance between the first and second maxima on the (O–O) RD slightly increases for the Na⁺ cluster and significantly decreases for the K⁺ and Cs⁺ clusters.

Based on the data of Table 2, the distributions of water molecules over the angle formed by the dipole moment of water molecule and the direction to the ion were plotted for the first and second hydrate spheres and the intermediate region. The ion Na⁺ exhibits the

highest orientation action on the water molecules in the first and the second hydrate spheres. It is interesting that, in the intermediate region, the angle distribution for the orientation of water molecules is approximately the same for the clusters of all the above ions (Fig. 3).

The angle distributions of hydrogen bonds in the first hydrate sphere and intermediate region of the Cs⁺–63H₂O cluster for different lengths of hydrogen bonds is presented in Fig. *4*. As can be seen from this figure, there are pronounced maxima in the angle
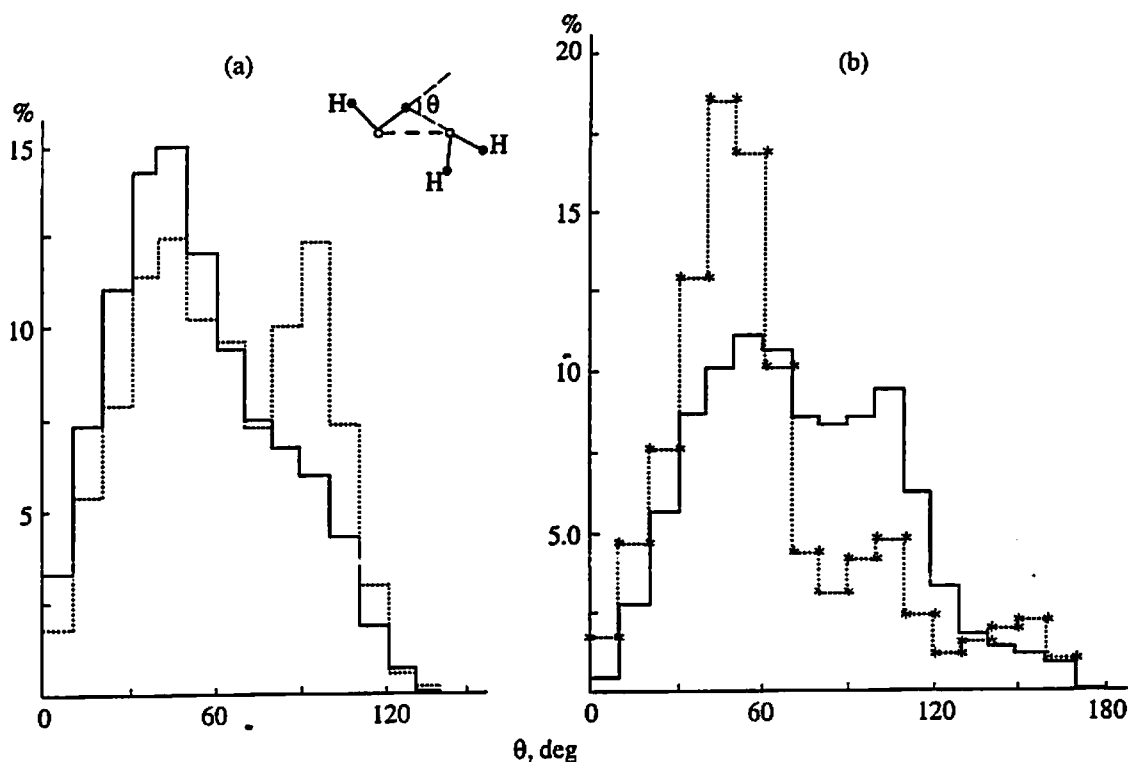
Fig. 5. Water molecules distribution over the hydrogen-bond angles in the K^+ clusters at O–O distance of 3.2 Å: dotted and solid lines correspond to clusters with 24 and 63 water molecules, respectively; (a) the first coordination sphere, (b) the intermediate region.

range 90° - 100°, which corresponds to the so-called bifurcating bonds, that is, the bonds in which one proton is involved in two hydrogen bonds [22, 23]. An important effect of these bifurcating bonds on the water molecule mobility in pure water was shown in [24, 25]. We explain a negative hydration of the K^+ ion by a large number of bifurcating bonds [5]. Figure 5 illustrates the changes in the angle distribution of hydrogen bonds in the K^+ cluster with increasing the number of water molecules. We used the inequality $r(O–O) < 2$ Å as a numerical criterion for the formation of hydrogen bonds during calculation. Note that the number of the bifurcate bonds decreases in the first hydrate sphere and increases in the intermediate region. For the Na^+ cluster, the number of bifurcate bonds is minimal.

Consider some dynamical characteristics of the hydration for the 24- and 63-water-molecule clusters. Table 4 displays the mean self-diffusion coefficients for water molecules in the clusters studied, which were calculated by formula

$$\overline{D} = \lim_{t \to \infty} \frac{1}{6t} \langle (r_i(t_0) - r_i(t_0 + t))^2 \rangle. \tag{2}$$

Unfortunately, the data presented are hardly comparable due to different temperatures being used in the numerical experiments. The frequency of water molecule transfer through the first minimum on the ion–oxygen RD and the lifetime of water molecules in the first hydrate sphere of ions are also presented in Table 4.

Despite the conditions of the above comparison, some conclusions can, nevertheless, be drawn from the data in Table 4. The lifetime of water molecules in the first hydrate sphere of the Na^+ ion is significantly higher than that for K^+ and Cs^+. The rate of water molecule exchange between the first and second hydrate spheres is significantly higher in the K^+ and Cs^+ clusters than in the Na^+ cluster. A comparison with similar data for pure

Table 4. Dynamic characteristics of the Na^+, K^+, and Cs^+ clusters

Cluster	$\overline{D}_{H_2O} \times 10^9$, m²/s	$k_{cross} \times 10^{-12}$, s⁻¹	$\tau \times 10^{12}$, s
Na^+–24H$_2$O (290 K)	4.0	2.0	15
Na^+–63H$_2$O (305 K)	7.0	1.4	15
Na^+–63H$_2$O (235 K)	1.0	0.8	50
K^+–24H$_2$O (290 K)	4.3	15.0	1.5
K^+–63H$_2$O (270 K)	1.6	12.8	2
Cs^+–24H$_2$O (285 K)	3.1		
Cs^+–63H$_2$O (285 K)	2.6	14.8	1.5

Note: $\overline{D}_{H_2O}$ is the mean diffusion coefficient of water molecules in a cluster; k_{cross} is the rate constant for a water molecule migration through the first minimum of the ion–oxygen RD; τ is the lifetime of a water molecule in the first coordination sphere of ion.

water [8] reveals a positive hydration for the Na⁺ ion and a negative hydration for the K⁺ and Cs⁺ ions. The mean self-diffusion coefficient of water molecules in the clusters considered is inconsistent with these data. Apparently, the studied clusters are too small to attain a reliable averaging of the water mobility.

In summary, the study of the structural and dynamical characteristics of water clusters of the Na⁺, K⁺, and Cs⁺ ions reveals a significant increase in the water molecule mobility near the K⁺ and Cs⁺ ions compared to that near the Na⁺ ion. An increase in the molecule mobility is explained by the formation of a large number of bifurcate bonds in the first hydrate sphere and in the intermediate range between the hydrate spheres of the K⁺ and Cs⁺ ions; in the case of the K⁺ cluster, the bifurcating bonds migrate from the first hydrate sphere to the intermediate region as the number of water molecules is increased. Apparently, solution conditions would make for a higher mobility of water molecules in the second hydrate sphere of the K⁺ ion rather than in the first one, in accordance with the model calculations [26]. A decrease in the mean self-diffusion coefficient of water molecules when passing from Na⁺ to Cs⁺ clusters is due to the small sizes of the clusters, in which the ion–water interaction energy decreases in the same sequence while H₂O–H₂O bond strength increases. The appearance of bifurcating bonds may be considered as defects in the network of water hydrogen bonds formed by rather large single-charged ions.

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