ISSN 1541-308X, Physics of Wave Phenomena, 2023, Vol. 31, No. 3, pp. 141–150. © Allerton Press, Inc., 2023.

STRUCTURING AND PHASE TRANSITIONS IN AQUEOUS SOLUTIONS

Structural and Spectral Signatures of Alkali Metal Ions in Water Clusters[1]

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Received January 23, 2023; revised January 23, 2023; accepted January 25, 2023

Abstract—Analysis of the results of nonempirical simulations of $Met^+(H_2O)_n$ clusters with Met = Li, Na, and K, and $n = 20–55$ carried out at the density functional level with B3LYP exchange-correlation functional and extended double-zeta basis sets revealed the prevailing structure motifs of the aqua complexes of alkali metal ions and their fingerprints in the infrared absorption spectra in the range of 2000–4000 cm^{-1}. The hydration structures of the ions are found to be predetermined by the balance between the conjugated H-bonded rings and extended ordered H-bonded sequences. The extension of the latter is shown to decrease with an increase in the effective radius of the ion, which is reflected in the stronger localization of the coupling of OH oscillators within the homodromic structural rings and the respective shift in the characteristic frequencies within the OH stretching domain.

Keywords: aqua complexes of alkali metal ions, hydration structures, hydrogen bonds, conjugation, coupled vibrations, infrared absorption spectra, OH band

DOI: 10.3103/S1541308X23030068

1. INTRODUCTION

It is long since the classification of ions as chaotropic and cosmotropic appeared. Another nomenclature uses structure-breaking and structure-making notions for the same particles. In any variant, particles of the former kind are assumed to distort somehow the water structure, while the latter are believed to produce some structuring effect. However, what effects are produced by the particles of both kinds? What are the peculiarities that determine the corresponding static and dynamic characteristics of the systems? Does the structuring support the inherent water structure or introduce some alternative organization motifs? Does the chaotropic effect actually consist in the distortion or breakage of the inherent structure? All the questions are theoretically interesting and, at the same time, practically important, since the proper consideration of all the related aspects sheds light on the microscopic organization of solutions.

Alkali metal ions, or more accurately the first three of them, namely, lithium, sodium, and potassium, seem to be very good candidates for such consideration. The vast literature devoted to experimental studies of aqueous solutions of various their salts along with numerous theoretical investigations of $Met^+(H_2O)_n$ ensembles (Met = Li, Na, K) that cover a broad range from the smallest clusters to periodic and extended aperiodic agglomerates gives much information about the static and dynamic properties of the systems. Furthermore, the ions are very convenient solutes as monoatomic particles of the same charge but varying size, which makes it possible to analyze changes in the local organization of water molecules around them taking into account not as many molecules sufficient for the formation of two solvation shells.

According to a conventional point of view, lithium ion is treated as structure-making, potassium ion as structure-breaking, while sodium ion occupying a so-to-speak transient position seems closer to structure-making agents. On one hand, it is natural that a small ion like lithium with a relatively high charge density should provide the strongest electrostatic effect on the neighboring water molecules, because the field intensity is sufficiently high beyond its formal ionic sphere. At the same time, potassium ion with the largest (among the ions considered) formal ionic radius produces a much weaker potential beyond its apparent boundary sphere, which should result in a weaker coordinating effect on water molecules, the number of which is larger within the first solvation shell due to its larger radius. Then, the idea of additional ordering and disordering (if this is an interpretation of cosmotropic and chaotropic concepts) seems quite natural for the

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[1] The text was submitted by the author in English.

ions. But here a question arises: if some ion acts as a strong coordinating site, then what kind of changes in the arrangement of molecules takes place upon its appearance “inside” a water cluster or droplet? Does the prevailing orientation of molecules around it become drastically different from that typical of individual water agglomerates? If yes, then one should speak about restructuring rather than simply structuring effect. Similarly, when the ion dissolved is relatively large, how does it affect the layers of surrounding molecules? Does it distort the H-bond network so strongly that can be treated as a destructuring agent (the one that introduces “chaos”)? Or does it introduce a moderate perturbation, which is reflected in a certain change in the mutual arrangement of surrounding molecules by promoting the prevalence of previously untypical or less probable structural motives? In the latter case, there is again no reason to speak about structure-breaking effect rather than restructuring. In both situations, the flexibility of the H-bond network close to the ion should be changed due to the coordinating effect of the latter, and the character of the change should be different for the ions of two kinds. These are the main topics we are going to touch in the paper.

To begin with, let us sum up the information about hydration of the ions. Lithium ion is a very convenient particle, since its nucleus has different isotopes, which makes it possible to study its solutions with the use of both X-ray and neutron scattering with an isotopic substitution in the latter case. Furthermore, its both strongly diluted and highly concentrated solutions can be prepared and investigated experimentally. Therefore, information about lithium ion hydration is broader compared to sodium and potassium. According to quite accurate X-ray diffraction data obtained by mid-seventieth and reviewed in [1], the first hydration shell of Li^+ involves four (4 (±1)) molecules at various concentrations of aqueous lithium chloride and sulfate solutions (2.22 m Li_2SO_4 [2], 6.86–18.5 m LiCl [3–5]) and six (or four to six) in bromide and tetrafluoroborate solutions (10.4 m $LiBF_4$ [6], 2.1 and 5.6 N LiBr [7]). Li–O distances were estimated as falling in the range of 1.95–2.25 Å. Neutron diffraction studies predicted the coordination number (*CN*) of Li in LiCl at a concentration of 9.98 m to be 3 ± 0.5 at an r(Li–O) distance of 1.95 ± 0.02 Å [1]. Later experiments (discussed in [8]) showed that the hydration shell composition of Li depends on the solution concentration and varies from 6.5 molecules at low concentrations to 3.2 in 14 m solution [9, 10]. Relatively recent data derived from neutron diffraction and isotopic substitution (NDIS) for the hydration structure of Li^+ in aqueous solutions of lithium chloride and lithium sulfate in heavy water (D_2O) showed [11] that the first hydration shell of Li^+ comprises on the average 4.3, 4.9, and 4.8 water molecules in 6, 3, and 1 m LiCl solutions, and 5.0 water molecules in 1.5 m Li_2SO_4 solution.

It is worth noting that four to six molecules are also typical of the close neighborhoods of sodium and potassium ions. For instance, according to X-ray and neutron diffraction studies of moderately concentrated aqueous solutions of sodium salts, a mean *CN* of Na^+ ion is 4.9 in 4 m $NaClO_4$ [12] and 5.1 in 3 m NaCl [13]. Similar but earlier experiments for potassium salt solutions enabled the same research group to estimate *CN*(K^+) as 5.3 in 4 m KCl. Quite recent XRD experiments [14] provided the *CN* value of sodium of 5.5 ± 0.3 and 5.9 ± 0.6 in 6 m and 2.6 m NaCl solutions in a reasonable agreement with the previous investigations, and mean Na–O distances of 2.384 ± 0.003 Å. The earlier estimates fell in the range of 2.41 to 2.42 Å [15]. Additionally, the dynamic Stokes radius of a sodium ion was estimated [16] to be 2.44 Å in aqueous NaCl solutions independent of the concentration in the range of 0.5 to 6 M based on the data of the pulsed field gradient NMR method. The latter value characterizes the hydration of sodium on a time scale about 1 μs, which is much larger compared to typical XRD or EXAFS scales; and the result obtained reflects the time-averaged size of the first hydration shell of sodium.

Thus, first-shell coordination numbers of lithium ion fall in the range of 4–6 depending on the composition of salts (the size and nature of the counterion) and their concentrations. In the case of sodium and potassium, the data scattering is broader, from 4 to 8 molecules in a close neighborhood of the ion (as summed up in [17]).

The spectrum of theoretical investigations of the hydration structures of alkali metal ions is very broad, from basic Hartree–Fock simulations of small clusters used particularly for creating effective potentials for molecular dynamics studies to extended stationary and dynamic calculations of large clusters in the second order of the Møller–Plesset perturbation theory (MP2) and at the density functional theory (DFT) level including combined quantum mechanical/molecular mechanical (QM/MM) modeling when the clusters are additionally surrounded with ensembles of water molecules described by sufficiently flexible force fields. We are not going to discuss all the data but briefly comment only the most spectacular ones.

For example, molecular dynamic simulations within the combined QM/MM approach when all molecules of the first and second solvation shells (within a spherical domain of an appropriate radius inside a cubic cell, which contained one lithium ion and 499 water molecules, with periodic boundary conditions) were described by the atomic basis set of a double zeta quality (DZP or DZP+) at the DFT level with a hybrid B3LYP functional, and the residual molecules were described with a BJH potential, the mean *CN* of lithium was estimated as 4.0–4.1, being slightly larger in the less flexible basis set [18, 19]. As a result of similar simulations supplemented with evolutionary algorithm for locating global minima followed by DFT-B3LYP and MP2 calculations with extended basis sets of double-zeta quality, the *CN*(Li) was found to be four in the global-minimum structures of $Li^+(H_2O)_n$ clusters with $n = 4–13$, 14, 15, and 20; five at $n = 17–19$; and as high as six at $n = 14$. The global minima corresponded to structures with the pyramidal rather than bipyramidal first hydration shells of lithium where the molecules were apparently gathered within one semi-sphere rather than "uniformly" arranged around the ion [20].

Recent study of the hydration shells of lithium ion by an example of $Li^+(H_2O)_n$ clusters ($n = 1–20$) simulated at the DFT level with *w*B97XD functional and 6-311++G(d,p) basis set with the effect of the surrounding water taken into account with the use of a polarizable continuum PCM model showed that the four-coordinated structure is favorable for the first hydration shell of lithium [21]. A mean *CN* of 4.1 to 4.2 was also found in the molecular dynamics studies of an ensemble of water molecules that contained a Li^+ ion with the use of QM/MM techniques; but the hydration structure of Li^+ was found to be quite flexible and water molecules in the first hydration shell to be relatively labile, so that pentacoordinate Li even originated, which was interpreted as not as high "structure-making" ability of the ion [22].

In QM/MM molecular dynamics simulations of Na^+ and K^+ hydration based on the Flexible Inner Region Ensemble Separator (FIRES) approach, when the ion and 12 nearest water molecules were represented by high level ab initio methods (RI-MP2/def2-TZVP and DFT-PBE/def2-TZVP), while the surrounding MM water molecules were represented by the polarizable SWM4-NDP potential, the ion coordination numbers were estimated to fall in ranges of 5.7–5.8 for Na^+ and 6.9–7.0 for K^+ [23].

To sum up, a widely accepted [24] point of view is that the driving force that determines the coordination of water molecules around the ions is of the electrostatic nature so that the short-range ion–water interactions that compete to those between water molecules govern the radial coordination of the latter around the ion (Li, Na, K), and the optimum first shell comprises four to six molecules arranged in vertices of a more or less distorted polyhedron unless the effective radius of the ion is large enough to make the first-shell molecules sufficiently labile to allow the involvement of additional ones in the shell, as in the case of a potassium ion, which is surrounded by eight molecules. However, this point of view as well as the aforementioned estimates for the first coordination sphere of the ions does not imply and reflect anything related to some peculiar structuring effects produced by the ions on the neighboring layers of water molecules. Is the varying lability of the molecules predetermined by their particular arrangement and respective correlation? This is the question addressed in the paper.

2. METHODICAL

To solve the problem formulated above, stationary nonempirical modeling of cluster systems composed of water molecules and alkali metal ions was selected as providing information about the local organization of the solvation shells of the ions and their dynamic characteristics reflected in the vibrational frequencies. A series of cluster structures of the following general composition $Met^+(H_2O)_n$ where Met = Li, Na, K and $n = 20–55$, was considered. The structures were constructed according to two approaches. In one variant, water molecules in threes or fives were successively added to smaller clusters to produce the larger ones. In another variant, the already found stable configurations of clusters were strongly distorted by substantially varying the water–water and Met–water distances, as well as the orientations of molecules. Upon modifications of both kinds, the arrangements of water molecules were optimized, and the resulting structures analyzed with a special attention to the peculiarities of hydrogen-bond networks.

Simulations were carried out at the density functional level (DFT) with a B3LYP hybrid exchange-correlation functional and a Gaussian-type double-zeta 6-31G basis set augmented with diffuse and polarization functions on lithium, sodium, oxygen, and hydrogen nuclei and a double-zeta basis set extended with (2d,p) functions combined with SBKJC core potential on potassium. For all the configurations identified as corresponding to stationary points of the potential energy, normal-coordinate analysis was carried out for two purposes, namely, to prove the correspondence of the structure to the potential minimum and to analyze the character and frequencies of vibrations in relation to the peculiarities of the hydrogen-bond network. For the analysis, the frequencies were scaled with a general factor of 0.96 that can be treated as quite reliable for the high-frequency range of stretching vibrations in the OH band of water that was of primary interest to us. To construct theoretical absorption spectra, the stick spectrum of a cluster was broadened with Lorentzian functions of an average width of 50 cm^{-1}, which was found to be quite reasonable as corresponding both to the possible thermal fluctuations within actual structures and the variability in the local arrangements of molecules in different clusters of the same molecular size.

Structural analysis was aimed at distinguishing the kinds of local coordination of water molecules depending on the number of hydrogen bonds they are involved in as proton donors (*d*) and acceptors (*a*) and local motives of the resulting hydrogen-bond network with a particular attention to the existence of its conjugated segments. According to our previous study [25], the formation of hydrogen bonds is chiefly predetermined by the lone-pair electrons (and orbitals) of individual molecules and, hence, the bonding has a combined σ/π character. Then, the alternation of covalent and hydrogen bonds like ...O–H...O–H...O–H... provides conditions for the delocalization of the corresponding bonding (H-bonding electrons), which has much in common with the usual π-conjugation in hydrocarbon molecules. As a result of this peculiarity of the electron density distribution, a certain correlation in the vibrational states of the molecules appears. It is manifested in the consistent oscillations of H-bond protons; and the more pronounced the conjugation of hydrogen bonds, the stronger the internal dynamic effects in the corresponding segments of the hydrogen-bond network.

When there appears a foreign particle in an ensemble of water molecules, it inevitably affects the states of the latter. The effect is the most pronounced in the case of the molecules involved in the first coordination shell of the foreign particle. When the particle is a charged ion, the molecules participate in the localization of its charge, which in the case of alkali metal ions is the electron density deficit; and the primary naturally expected manifestation of the interaction is the orientation of the molecular dipoles with their oxygens toward the metal ion. Such a reorientation inevitably affects the hydrogen-bond network at least in the close vicinity of the ion. The degree of the effect and its consequences depending on the nature of the ion (lithium, sodium, and potassium) are the main aspects discussed below.

3. RESULTS AND DISCUSSION

First of all, let us consider structures of $Met^+(H_2O)_n$ clusters, Met = Li, Na, K and $n = 20–55$, and distinguish possible variants of the water structure organization around the ions.

The smallest lithium ion characterized by the highest local charge density provides the strongest effect on the neighboring water molecules. Examples of $Li^+(H_2O)_n$ clusters with n = 27, 33, and 48 are shown in Fig. 1. As can be seen, the first hydration shell of lithium is not necessarily tetrahedral, but can involve five water molecules. Depending on the coordination number of lithium, the effective radius of its first hydration shell estimated as mean Li–O distances varies from 1.96 Å at $CN = 4$ to 2.12 Å at $CN = 5$. On the average, the LiOHH dihedral angles for all these molecules are about 120°, so that the predominant orientation of the molecules enables their effective involvement in the so-to-speak tangential structure elements of the hydrogen-bond network. These structure elements are typically four- and five-molecular rings. And a characteristic feature of such rings in the lowest-energy structures is the regular alternation of covalent and hydrogen bonds, which means that hydrogen bonds within such rings are ordered, having e.g. clockwise or counterclockwise orientation, and the rings can be classified as homodromic. The first-shell molecules can be involved in one or even two such rings. Furthermore, the complementary ordering of H-bonds within two fused rings (which have a common H-bond between a common pair of water molecules) extends the domain of H-bond delocalization or conjugation. It is interesting that in $Li^+(H_2O)_{27}$ cluster, which involves four first-shell and 23 second-shell molecules and, as such, can be considered as representing a situation when two nearly complete hydration shells are formed around the ion, there are only two molecules uninvolved in any conjugated ring. This cluster is most spectacular in this respect. In the residual clusters considered, the size diversity of conjugated rings is extended (from tri- to hexamolecular ones), while the fraction of water molecules involved in them becomes smaller, e.g., 82% in $Li^+(H_2O)_{33}$ and about two thirds at $n > 38$. However, a more important aspect is that starting from any molecule of the first hydration shell it is possible to construct a path along the conjugated sequence of hydrogen bonds that (including a few self-intersections) would cover the whole cluster and involve all the residual molecules of the first-shell. This means that all the molecules within at least the first two solvation shells are mutually related (or their states are correlated), and the relation between the molecules of the first shell is mediated by those of the second shell. The corresponding domain can already be thought of as quite extended, because in a 1 M solution of 1:1-electrolyte, there is about 56 molecules per both ion and counterion, which is by half smaller than in the largest cluster considered. Thus, even in 0.5 M lithium salt solutions, nearly all the water molecules can be expected to be involved in internally correlated domains provided that the counterion affects the water molecules at a comparable level.

Now, let us turn to the hydration structures of a sodium ion. Because of its larger effective radius and, hence, the lower effective charge density, its electrostatic effect on water molecules should be smaller. It is reflected in both the larger radius of the first solvation shell (and accordingly the larger number of molecules typically involved in it), and in the orientation of the molecules with respect to the Na–O lines. Further-

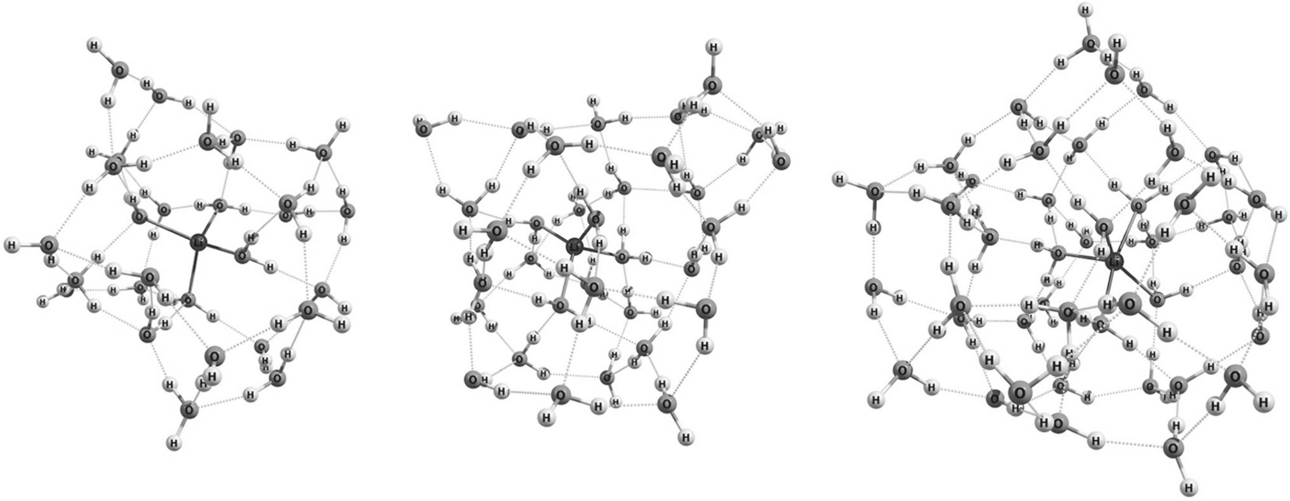

Fig. 1. Structures of model $Li^+(H_2O)_n$ clusters with $n = 27$, 33, and 43. Li–O coordination bonds within the first hydration shell are shown with solid lines for clarity.

more, interactions of water molecules when the number of the latter is sufficiently large can already partly counterbalance the effect of the sodium ion, so that the ion can reside either closer to the spatial center of the cluster or to its surface (Fig. 2). When the total number of water molecules around the ion is smaller than 30, which corresponds to the concentrations of 1 : 1-electrolyte solutions no lower than 1 M, the ion is pentacoordinate; when it increases above 45, which can be reached in ca. 0.5 M and more diluted sodium salt solutions, the ion becomes steadily hexacoordinate. When the hydration shell of sodium is noticeably thicker at one side and thinner at the other (which means that water–water interactions are on the whole energetically comparable to the effect produced by sodium, so that agglomeration of molecules at one side of the ion is energetically possible), the mean r(Na–O) distances are smaller compared to those characteristic of the clusters where sodium occupies nearly the spatially central position. The differences are about 0.02 Å at $n = 28$ or 43 and $CN = 5$ and about 0.02 to 0.03 Å at $n = 51$ and $CN = 6$. At the same time, the values themselves are smaller for the pentacoordinate neighborhood compared to the hexacoordinate one, though the absolute difference is smaller than that in the case of lithium hydration shells: ca. 2.42 vs. 2.46 Å for the central position of sodium in the cluster and 2.37 vs. 2.45 Å for the lop-sided structures. As to the H-bond networks formed in $Na^+(H_2O)_n$ clusters, the following features can be mentioned. In comparison to the lithium–water clusters, here, a still larger diversity in the sizes of molecular rings can be noticed, from tri- to heptamolecular ones; and the fraction of homodromic ones decreases with an increase in the cluster size. For example, it is only 5 of 28 water molecules in $Na^+(H_2O)_{28}$ cluster with CN(Na) = 5 that are not involved in conjugated H-bonded rings, most of which are homodromic, so that a substantial fraction of molecules is involved in the conjugated network elements, which on the whole cover the predominant part of the hydration structure. In $Na^+(H_2O)_{43}$ cluster with CN(Na) = 6, the number of molecules uninvolved in conjugated H-bonded rings increases to 13, which is about a third of the total number. However, all these molecules are involved in relatively extended and branched open conjugated sequences of hydrogen bonds that embrace the whole structure. At $n = 51$ and $CN = 6$, despite the visually large number of nonhomodromic rings in the H-bond network of the cluster, it is only 16 molecules, i.e., again about a third of the total number, which are not involved in any closed homodromic sequence of hydrogen bonds, but the sequences are either relatively small, tetramolecular, or relatively large, up to a folded octamolecular one. Generally, this trend is similar to the one noticed in the case of lithium hydration structures. But now construction of a continuous path along conjugated sequences of hydrogen bonds results in a 3D structure that is characterized by numerous repeatedly superimposed at least half-ring segments. This means that the correlation between molecules predetermined by their involvement in conjugated H-bond sequences becomes more localized within individual or adjacent and fused rings rather than uniformly extends over the whole structure.

Finally, if one turns to the hydration structures around the largest considered cation, potassium, it can be said that they inherit something from those of sodium ion, but at certain differences expectedly predetermined by the larger size of the potassium ion. For example, at the relatively small number of water molecules in the cluster, as in $K^+(H_2O)_{33}$, only three mol-

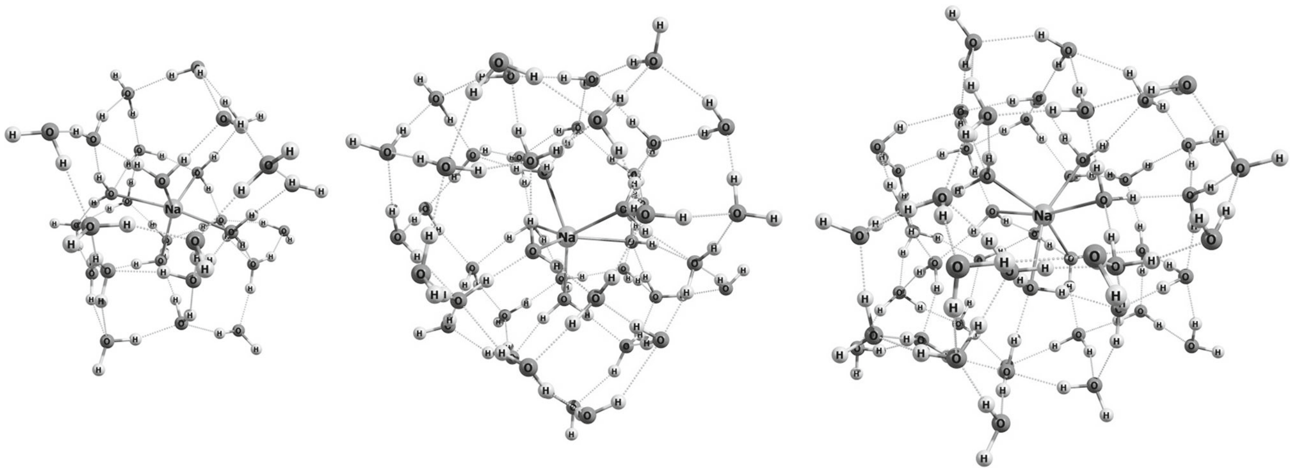

Fig. 2. Structures of model $Na^+(H_2O)_n$ clusters with $n = 28$, 43, and 51. Na–O coordination bonds within the first hydration shell are shown with solid lines for clarity.

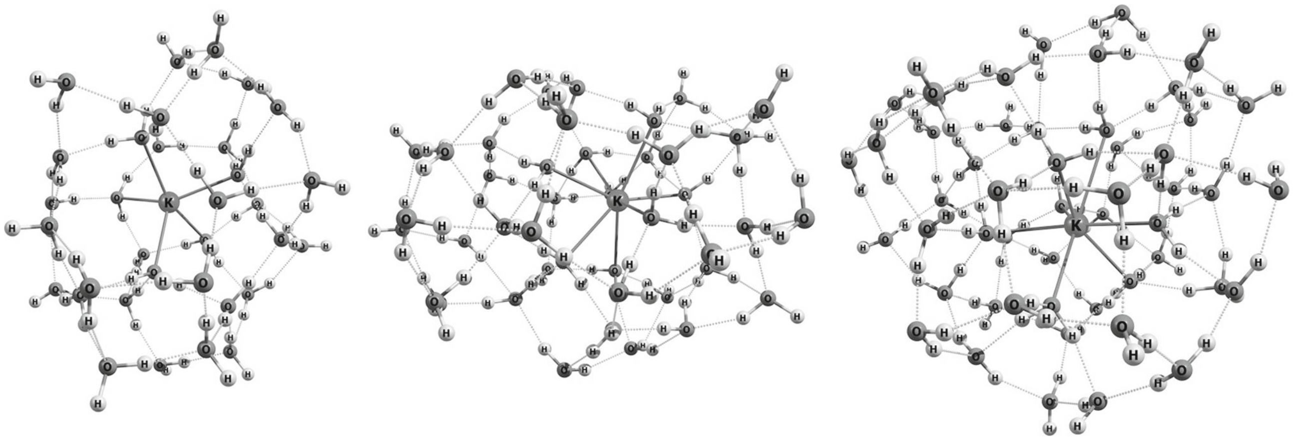

Fig. 3. Structures of model $K^+(H_2O)_n$ clusters with $n = 33$, 43, and 51. K–O coordination bonds within the first hydration shell are shown with solid lines for clarity.

ecules (and none of them from the first hydration shell) are not involved in homodromic rings stabilized by conjugated H-bond sequences, though two rings are as large as octamolecular ones, while all the residual are tetra- and pentamolecular. It is worth noting that in this cluster, there are five molecules in the first hydration shell at a mean K–O distance of 2.68 Å and one more at r(K–O) = 3.39 Å, 13 molecules within a relatively thin radial layer at a mean K–O distance of 4.29 Å and 14 molecules that constitute the next much looser layer at a mean r(K–O) = 5.47 Å. Already this scope of figures shows that the organization of the structure is much less pronounced compared to those formed around lithium and sodium where the scattering in the Met–O distances for the first-shell molecules typically fell in ranges of 0.05–0.10 Å in the case of Li and 0.05–0.25 Å in the case of Na irrespectively of the molecular size of the cluster. When the number of water molecules in the hydration sphere of potassium is increased by ten, the percentage of molecules uninvolved in homodromic rings increases to 25%, which is again visually smaller than the values typical of both lithium and sodium hydration clusters, but the drastic difference to the latter ones is that two thirds of the first-shell molecules are of this kind. This means that despite the generally extended conjugated domain that covers the whole cluster, the actual correlation within the first-shell molecules is very weak. Furthermore, any attempt to construct a continuous path along conjugated H-bond sequence fails as coming to a closed ring with no additional routes out. This means that the trend noticed in sodium clusters becomes more pronounced in the potassium hydration structures: the whole structure can be divided into spatial domains within which the correlation between molecules is relatively strong, but the correlation between the domains is weak.

The stronger the correlation between molecules, the lower should be the vibrational frequencies of H-bond protons in the structures and the more delocalized should be the corresponding vibrations as involving concurrent and consistent oscillations of a number of the protons. And here a balance or a competition between the two kinds of correlation distinguished on the basis of the structural analysis can be expected, namely, a correlation within closed rings and a correlation within segments of extended open conjugated paths. The roles of these variants should vary depending on the chemical nature of the alkali metal ion.

The theoretical vibrational spectra of lithium ion aqua complexes in the high-frequency OH-range are different depending on the coordination number of lithium. In the case of $CN = 4$, the band is broad with a series of absorption peaks that can conditionally be considered as successive waves. In the case of $CN = 5$, there is quite a pronounced drop in absorbance around 3100–3180 cm^{-1}. The lower-frequency part of the OH-absorption band is predetermined by the vibrations of several H-bond protons that belong either to the same conjugated H-bonded ring or two adjacent homodromic rings. In most situations, the largest contribution to the corresponding normal coordinates is provided by the shifts of the protons of the second-shell molecules. However, in particular situations protons of the first-shell molecules can also be involved with noticeable weights in the corresponding effective vibrational coordinates, and in these situations, the predicted intensity of the spectral signal substantially increases. The low-frequency tail of the OH-band can start at as low frequencies as 2600 cm^{-1} when $CN(\text{Li}) = 5$ and around 2850–2900 cm^{-1} when $CN(\text{Li}) = 4$. The higher-frequency part of the OH-absorption band is predetermined by the oscillations of H-bond protons, which are involved in conjugated sequences that are composed of segments of two to four homodromic rings. The sequences look like zigzag chains, and when the number of consistently oscillating H-bond protons becomes relatively large, a higher absorbance is observed in a 3250–3450 cm^{-1} range. Here, the chains can be as long as ten- or twelve-molecular. As an example, the absorption spectrum of $\text{Li}^+(\text{H}_2\text{O})_{33}$ cluster is shown in Fig. 4a.

In $\text{Na}^+(\text{H}_2\text{O})_n$ clusters, the OH-absorption band is visually broader with a relatively extended lower-frequency part where the absorbance is not regularly growing with an increase in frequency. This part is conditionally separated from the next, higher-frequency one by a more or less pronounced drop in absorbance around 3050–3070 cm^{-1}. Within the former part, the signals are predetermined by the activation of oscillations of molecules involved in tetra- and pentamolecular rings with the highest contribution from those which are double acceptors and single donors in the H-bonds with the neighbors. And the higher absorbance corresponds to the vibrations typically in pairs of rings that are coupled either via a common vertex molecule or a bimolecular bridge. Within the latter, higher-frequency part of the band, the largest contributions to signals are due to the absorption by OH oscillators in homodromic molecular rings bound to a common molecular chain that involves molecules of the first hydration sphere of the sodium cation. The highest absorbance is observed within the range of 3150–3400 cm^{-1}. As an example, theoretical absorption spectrum of $\text{Na}^+(\text{H}_2\text{O})_{48}$ cluster is shown in Fig. 4b.

In $\text{K}^+(\text{H}_2\text{O})_n$ clusters, most of the closed conjugated structure elements are tetra- and pentamolecular rings. They are not as numerous; and the correlation in vibrational states of the corresponding molecules is restricted to these very rings. Accordingly, there are typically few signals in the vibrational absorption spectra of the clusters with the frequencies as low as 2400–2700 cm^{-1}, which correspond to oscillations of H-bond protons in the molecules that are vertices of individual homodromic pentamolecular rings. Then, after a certain drop in absorbance, the range of 2800 to 3100 cm^{-1} can be distinguished where oscillations of H-bond protons that belong to tetra-, penta-, or hexamolecular rings with an involvement of the protons of one or two first-shell molecules are activated. Finally, a broad band in the range of ca. 3260–3460 cm^{-1} with a maximum absorbance close to 3300–3350 cm^{-1} corresponds to relatively delocalized oscillations to which molecules of the first hydration shell contribute noticeably. As an example, the predicted spectrum of $\text{K}^+(\text{H}_2\text{O})_{43}$ cluster is shown in Fig. 4c.

To sum, we can state that with an increase in the effective radius of the ion and, hence, an increase in the first hydration shell radius at a concurrent decrease in the direct effect of the ion on the orientation of water molecules within this shell, the OH-absorption band of the vibrational spectrum is found to extend to the lower frequencies, where oscillations of H-bond protons within conjugated molecular rings are activated. The smaller the radius of the ion and the stronger the effect it produces on the neighboring water molecules, the less localized the conjugated H-bonded domains and the higher the lowest OH-band frequencies. Furthermore, this lower-frequency part of the OH absorption band becomes less clearly separated from the higher-frequency part with an increase in the size of the cation.

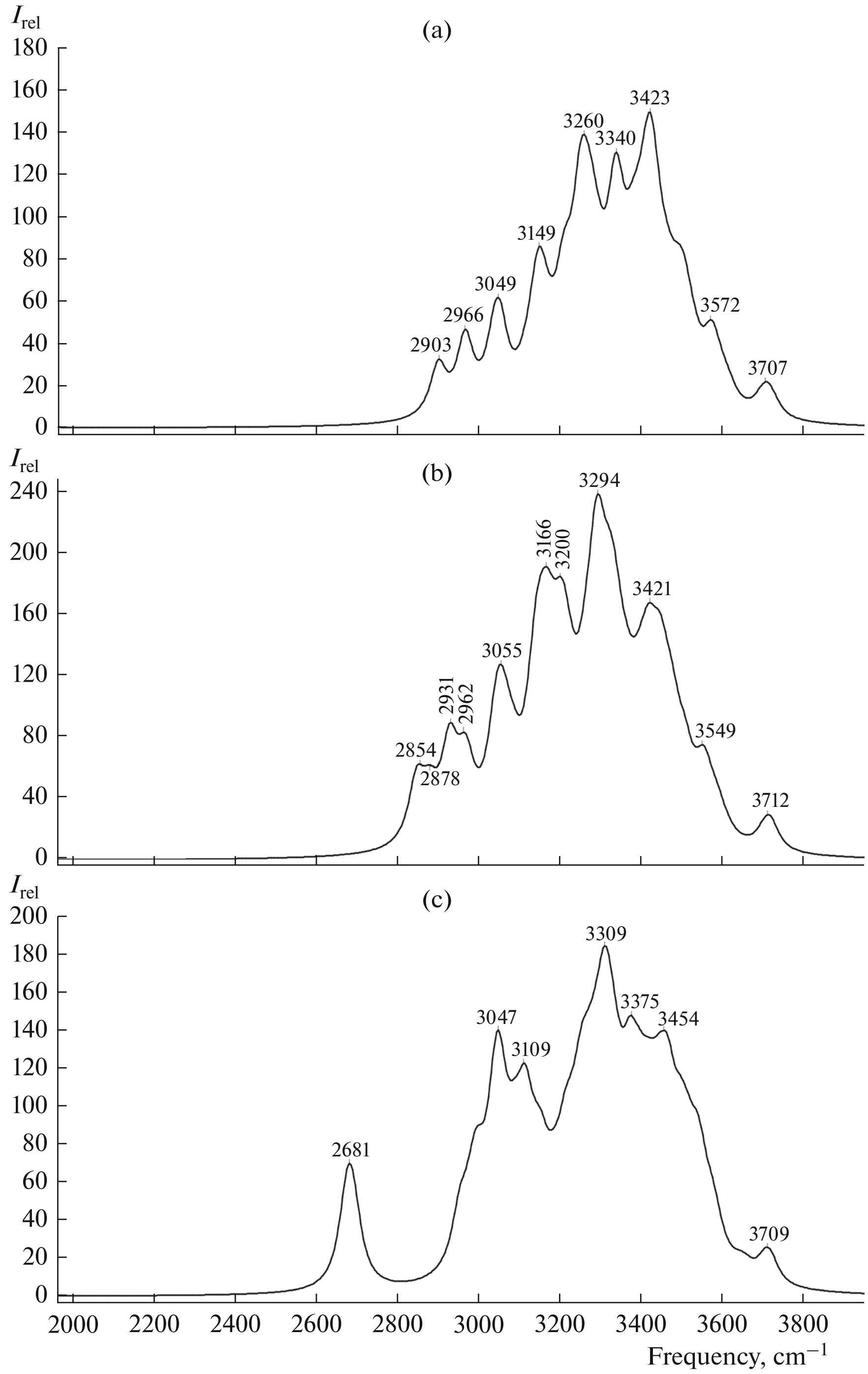

Fig. 4. OH absorption bands of the theoretical infrared absorption spectra of (a) $Li^+(H_2O)_{33}$, (b) $Na^+(H_2O)_{48}$, and (c) $K^+(H_2O)_{43}$ clusters.

4. CONCLUSIONS

Nonempirical simulations of diverse cluster structures composed of water molecules and a foreign alkali metal ion, lithium, sodium, or potassium, enable us to judge the dependence of the character of the H-bond network formed on the relative effective size of the ion and, hence, on the relative excess charge density, in the localization of which water molecules are substantially involved. The smaller the ion and the higher the local charge density, the more regular the H-bond network formed around the ion. Around lithium, almost all the molecules including those of the first hydration shell of the ion are involved in the common hydrogen bond in such a way that it is possible to construct a continuous path covering the whole structure with not as many overlapping segments. With an increase in the effective size of the cation and a respective decrease in the local excess charge density, the more restricted the correlation in the states (particularly, vibrational states) of the molecules in the cluster is, so that local homodromic rings can easily be distinguished, but a continuous ordered H-bond path either involves numerous repeatedly overlapping segments as in the case of sodium or is restricted to certain parts of the whole structure so that segments of the lower molecular dimensionality can apparently be separated as in the case of potassium. Accordingly, the degree of coupling between the OH oscillators, or, in other words, the delocalization of vibrations changes depending on the spatial domains where the correlation between molecules takes place. As a consequence, the vibrational frequencies also change, being lower in the case of the highly correlated and localized oscillations of OH groups within homodromic molecular rings and higher in the case of the coupled shifts of the H-bond protons within extended chains that can involve both first-shell molecules and segments of homodromic rings.

Thus, there is a regular trend predetermined by the effective radii of the foreign ions, which is reflected in the competition of the structure motives, which are localized homodromic rings and branched conjugated H-bond sequences. Their contributions to the overall structure and the absorption of infrared radiation change so that both play a substantial role in the case of lithium, while the former become gradually prevailing in the solvation shells of the larger cations, sodium and potassium.

CONFLICT OF INTEREST

The author declares that she has no conflicts of interest.

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