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Emergence of Solvent-Separated Na^+–Cl^- Ion Pair in Salt Water: Photoelectron Spectroscopy and Theoretical Calculations

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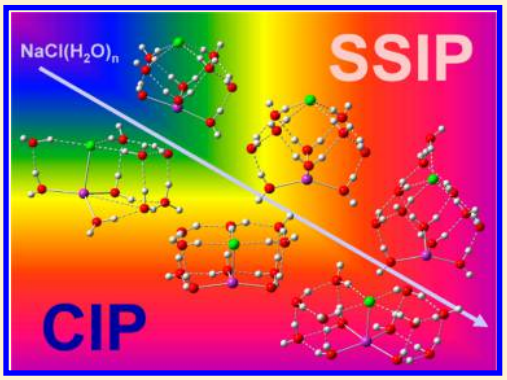
Supporting Information

ABSTRACT: Solvation of salts in water is a fundamental physical chemical process, but the underlying mechanism remains unclear. We investigated the contact ion pair (CIP) to solvent-separated ion pair (SSIP) transition in $NaCl(H_2O)_n$ clusters with anion photoelectron spectroscopy and ab initio calculations. It is found that the SSIP type of structures show up at $n = 2$ for $NaCl^-(H_2O)_n$ anions. For neutral $NaCl(H_2O)_n$, the CIP structures are dominant at $n < 9$. At $n = 9$–12, the CIP structures and SSIP structures of $NaCl(H_2O)_n$ are nearly degenerate in energy, coincident to the H_2O:NaCl molar ratio of NaCl saturated solution and implying that the CIP and SSIP structures can coexist in concentrated solutions. These results are useful for understanding the solvation of salts at the molecular level.



Salt ions can strongly affect the structural and dynamical properties of water hydrogen bonding network.[1] They also play diverse roles in the Hofmeister series and biochemical systems.[2−5] To understand the effects of salt ions on water as well as their correlation with the Hofmeister series,[1,6] it is especially important to investigate the contact ion pair (CIP) to solvent-separated ion pair (SSIP) transition in salt water[7,8] and the arrangement of water molecules in the first solvation shell. Many efforts have been devoted to understanding the solvation of salts in water.[9−16]

Sodium chloride (NaCl) is the most common and simplest salt. It is not only important in atmospheric chemistry,[17] biochemistry,[18] and our daily life, but also a basic model system for understanding the solvation of salts in water. In the last decades, many theoretical studies including ab initio calculations,[19−26] Monte Carlo simulations,[27−29] and molecular dynamics simulations[30−41] have been performed on $NaCl(H_2O)_n$ clusters or aqueous NaCl solutions. The structural properties of NaCl saturated aqueous solution were explored by an X-ray diffraction experiment.[42] The NaCl–H_2O complex was studied by Ar-matrix isolated infrared spectroscopy.[43] The $NaCl(H_2O)_n$ clusters in the size range of $n = 1$–3 were investigated by Fourier transform microwave (FTMW) spectroscopic experiments,[44,45] those in the range of $n = 1$–4 investigated by infrared spectroscopy in liquid helium nanodroplets,[46] and those of $n = 150$–400 by X-ray photoelectron spectroscopy.[47] Recently, the $(NaCl)_3(H_2O)_n$ ($n = 0$–6) clusters were investigated by anion photoelectron spectroscopy and theoretical calculations.[48]

Despite extensive theoretical and experimental studies in the last four decades, the number of water molecules needed to induce SSIP for NaCl is still under debate, and the detailed structures of hydrated NaCl near the CIP–SSIP transition region remain unknown. In this work, we studied the initial solvation process of NaCl in water by mass-selected anion photoelectron spectroscopy of $NaCl^-(H_2O)_n$ clusters and ab initio calculations. Brute force theoretical calculations have been employed to explore the transition between CIP and SSIP structures. The results show that the CIP structures and SSIP structures of $NaCl(H_2O)_n$ at $n = 9$–12 are nearly degenerate in energy, indicating the CIP and SSIP structures may coexist in concentrated solutions.

The photoelectron spectroscopy experiments of mass-selected $NaCl^-(H_2O)_n$ clusters were conducted on a home-built apparatus.[49] (See the Supporting Information for more details.) Figure 1 presents the photoelectron spectra of $NaCl^-(H_2O)_n$ ($n = 0$–6) clusters measured with 1064 and 532 nm photons. The verticle detachment energies (VDEs) and adibatic detachment energies (ADEs) of $NaCl^-(H_2O)_n$ ($n = 0$–

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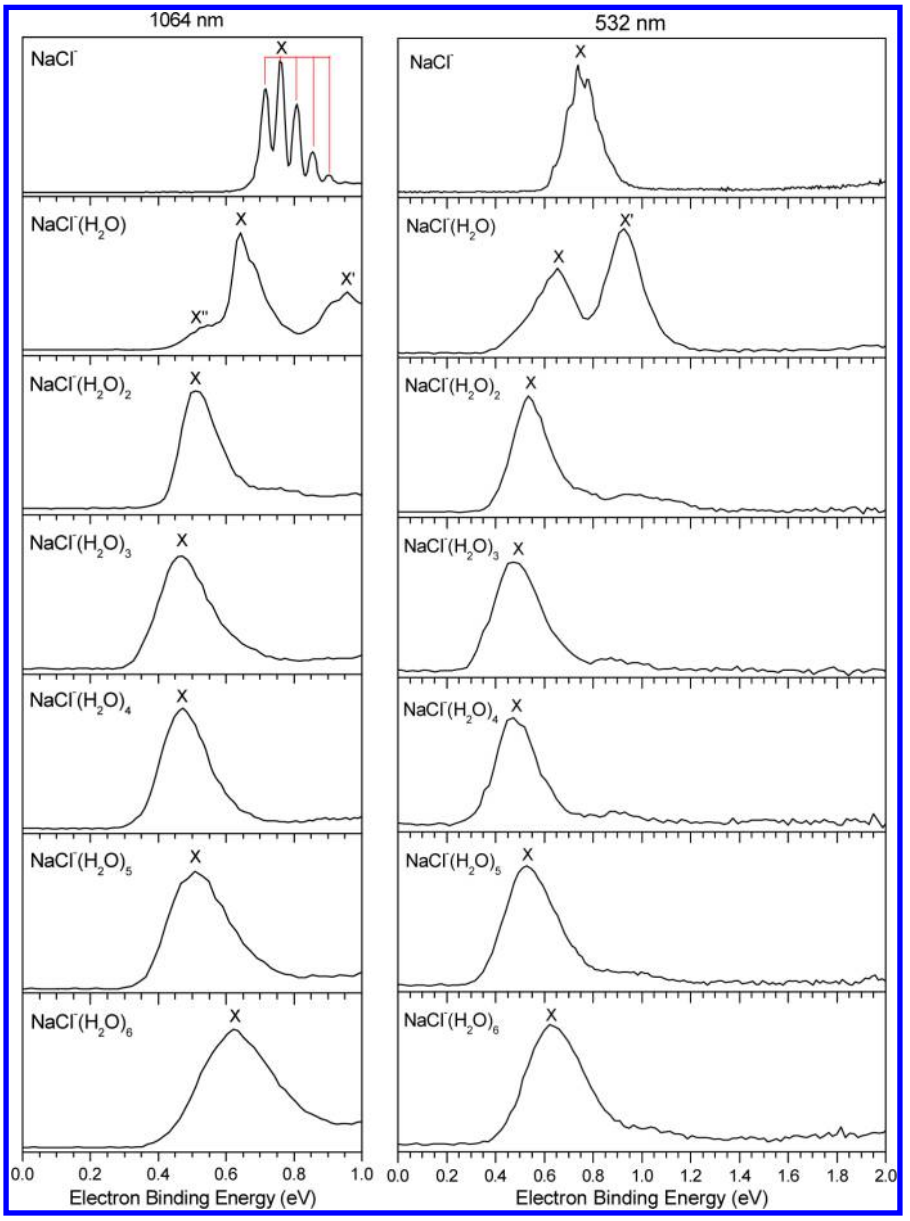

Figure 1. Photoelectron spectra of $NaCl^-(H_2O)_n$ (n = 0–6) clusters measured with 1064 and 532 nm photons.

Table 1. Experimental VDEs and ADEs of $NaCl^-(H_2O)_n$ (n = 0–6)[a]

	X		X′		X″	
$NaCl^-(H_2O)_n$	ADE (eV)	VDE (eV)	ADE (eV)	VDE (eV)	ADE (eV)	VDE (eV)
0	0.717(10)	0.762(10)				
1	0.63(8)	0.64(8)	0.86(8)	0.96(8)	0.46(10)	0.54(10)
2	0.46(8)	0.51(8)				
3	0.36(8)	0.46(8)				
4	0.38(8)	0.48(8)				
5	0.39(8)	0.52(8)				
6	0.45(8)	0.63(8)				

[a]The numbers in the parentheses indicate the experimental uncertainty in the last digits.

6) clusters estimated from their spectra are summarized in Table 1.

The photoelectron spectrum of $NaCl^-$ at 532 nm shows a partially resolved broad feature centered at about 0.74 eV, which is clearly resolved into five fine structures with an even spacing of 375 ± 40 cm^{-1} in its 1064 nm spectrum. These fine structures correspond to the vibrational progression due to the excitation of the Na–Cl stretch of the neutral NaCl, in good agreement with the infrared spectroscopy experiment.[50] The ADE of $NaCl^-$ (electron affinity of NaCl) is determined to be 0.717 ± 0.010 eV from the resolved 0–0 transition, also in agreement with an earlier experiment.[51]

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The spectrum of $NaCl^-(H_2O)$ measured with 532 nm photons shows two major features (X and X′) centered at about 0.64 and 0.96 eV, respectively. In addition, there is a slow rising shoulder (X″) at the low binding energy region (~0.54 eV), which is more apparent in the 1064 nm spectrum. The relative intensities of X, X′, and X″ are experimental condition-dependent (Figure S2), indicating that the X and X′ features may come from two different isomers, and X″ may come from a third one.

The spectrum of $NaCl^-(H_2O)_2$ recorded with 1064 nm photons has a broad feature (X) centered at ~0.51 eV. Its 532 nm spectrum shows an additional small feature at ~0.99 eV which is likely due to the O−H stretch of water molecules, similar to that observed in $LiI^-(H_2O)_n$ clusters.[52] The spectra of $NaCl^-(H_2O)_n$ with n = 3−6 each has a major broad feature (X). The VDE of $NaCl^-(H_2O)_3$ is measured to be 0.46 eV, and that of $NaCl^-(H_2O)_4$ is 0.48 eV. Similar to the case of $NaCl^-(H_2O)_2$, the 532 nm spectra of $NaCl^-(H_2O)_3$ and $NaCl^-(H_2O)_4$ each has a small peak at about 0.9 eV, which can be attributed to the O−H stretch of water molecules (Figure S3). The VDEs of $NaCl^-(H_2O)_5$ and $NaCl^-(H_2O)_6$ are 0.52 and 0.63 eV, respectively, and both of their 532 nm spectra have small tails. The broad features observed in the spectra indicate that multiple isomers may coexist in the experiments. Similar to the cases of $LiI^-(H_2O)_n$ and $CsI^-(H_2O)_n$ clusters,[52] the decrease of the VDEs for $NaCl^-(H_2O)_n$ from n = 0 to 3 probably indicates that the first three water molecules mainly interact with the Na atom, while the increase of VDEs from n = 4−6 implies that the fifth and sixth water molecules mainly interact with the Cl atom and/or with the other water molecules via hydrogen bonds.

We conducted theoretical calculations on $NaCl^-(H_2O)_n$ anions and their neutral counterparts to compare with the expeirment. The structures of $NaCl^{-/0}(H_2O)_n$ clusters were generated with the integrated tempering sampling (ITS)[53] molecular dynamics and were fully optimized with density functional theory (DFT) calculations employing the long-range corrected hybrid functional LC-ωPBE[54] as implemented in the *Gaussian 09* program package.[55] The Pople's all-electron basis set 6-311++G(d, p)[56] was used for all the atoms. More accurate single-point energies were obtained with the CCSD(T)[57] and MP2[58] methods with very large basis sets, such as aug-cc-pVTZ[59,60] and maug-cc-pVTZ.[61]

The Na−Cl bond length of $NaCl^-$ anion is calculated to be 2.507 Å. The VDE and ADE of $NaCl^-$ are calculated to be 0.736 and 0.717 eV, respectively, in agreement with the experimental values of 0.762 and 0.717 eV. The typical low-lying isomers of $NaCl^-(H_2O)_n$ (n = 1−6) are presented in Figure 2 (more structures can be found in the Supporting Information).

$NaCl^-(H_2O)$ has three isomers close in energy. The first isomer has H_2O interacting with both Cl and Na; the second one has H_2O interacting with Cl only; while the third one has H_2O interacting with Na only. The most stable isomer (1A) can be considered as a Cl−water−Na ring (NaCl-1W ring), in which the O atom of H_2O connects to the Na atom and one H atom of H_2O interacts with the Cl atom to form a hydrogen bond, and the other H atom of H_2O is slightly out of the ring plane. Isomer 1B has a quasi-linear Na−Cl···H−O configuration with the water molecule interacting with the Cl atom through a hydrogen bond. Isomer 1C has a C_{2v} symmetry with the water molecule connecting to NaCl via the Na−O interaction. The VDEs of isomers 1A, 1B, and 1C are calculated

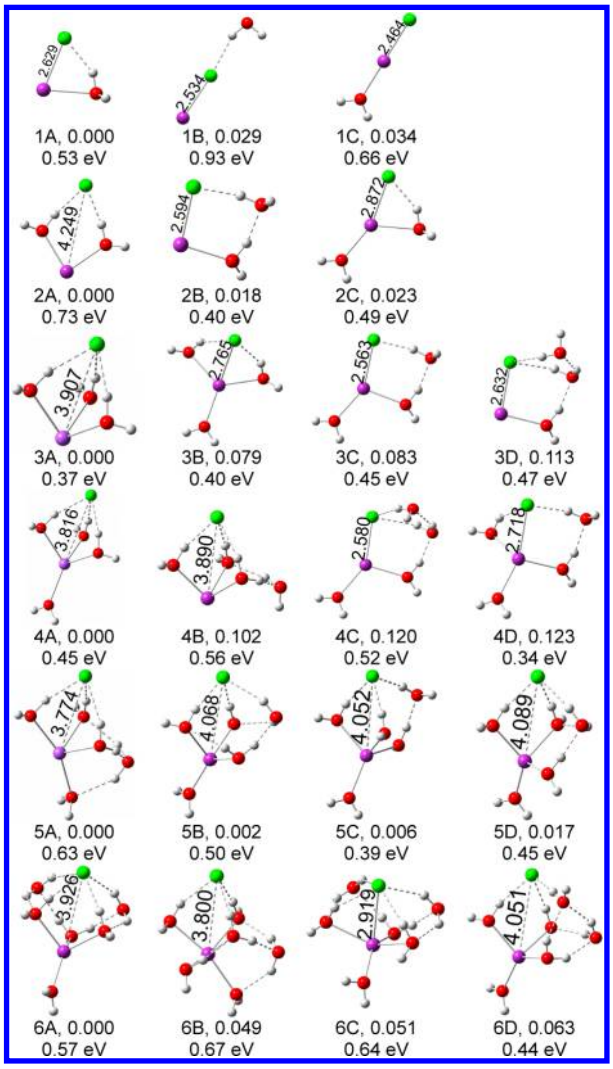

Figure 2. Typical low-lying isomers of $NaCl^-(H_2O)_n$ (n = 1−6). The theoretical VDEs are shown under the relative energies (in electronvolts). The Na−Cl distances (in angstroms) are also labeled. The relative energies and theoretical VDEs of $NaCl^-(H_2O)_{0-4}$ were calculated at the CCSD(T)/aug-cc-pVTZ//LC-ωPBE/6-311++G-(d,p) level of theory, and those of $NaCl^-(H_2O)_{5-6}$ were calculated at the CCSD(T)/maug-cc-pVTZ//LC-ωPBE/6-311++G(d,p) level of theory. The purple and green balls stand for the Na and Cl atoms, respectively.

to be 0.53, 0.93, and 0.66 eV, respectively, which are in good agreement with the X″, X′, and X features in the experimental spectra, implying that all three isomers coexist in our experiment.

Similarly, $NaCl^-(H_2O)_2$ has three isomers nearly degenerate in energy. The most stable isomer (2A) has two NaCl-1W rings, which share the same Na···Cl edge. The Na−Cl distance increases significantly to 4.249 Å compared to that of 2.507 Å in bare $NaCl^-$ and 2.629 Å in $NaCl^-(H_2O)$. Isomer 2B has a Cl−water−water−Na ring (NaCl-2W ring) structure, in which the two water molecules connect to each other through a hydrogen bond, and one of them interacts with Na through its O. The other water forms a hydrogen bond with the Cl atom. Isomer 2C has a NaCl-1W ring, and the second water molecule connects to the Na atom via Na−O interaction. The calculated VDEs of these isomers are all in reasonable agreement with the

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experiment. Considering the small differences of their energies, they may coexist in the experiment.

The most stable structure of $NaCl^-(H_2O)_3$ (3A) is composed of three NaCl-1W rings sharing the same Na···Cl edge. The Na−Cl distance in isomer 3A is 3.907 Å, slightly shorter than that in isomer 2A (4.249 Å). Its VDE is calculated to be 0.37 eV, in reasonable agreement with the experimental value of 0.46 eV. Isomers 3B, 3C, and 3D are higher in energy than 3A by 0.079, 0.083, and 0.113 eV, respectively. Their structures can also be characterized by the existence of NaCl-1W rings or NaCl-2W rings. Isomer 3B may be derived from 2C, while 3C and 3D can be derived from 2B by addition of the third water to the Na or Cl side, respectively. The populations of isomers 3B, 3C, and 3D in the cluster beam might be very low because they are higher in energy than 3A by at least 0.079 eV.

The most stable structure of $NaCl^-(H_2O)_4$ (4A) is composed of three NaCl-1W rings similar to that in isomer 3A and has the fourth water molecule interacting with the Na atom via its O atom from the opposite side of the Cl atom. The calculated VDE of isomer 4A is in good agreement with the experimental value. Isomers 4B−4D can also be characterized by the formation of NaCl-1W rings or NaCl-2W rings derived from the smaller clusters by addition of water to different positions. It is unlikely for them to be present in the cluster beam because they are higher in energy than isomer 4A by 0.102, 0.120, and 0.123 eV, respectively.

It appears that the formation of triple NaCl-1W rings in $NaCl^-(H_2O)_3$ and $NaCl^-(H_2O)_4$ makes the most stable isomers much lower in energy than the other isomers. At n = 5 and 6, the added water molecules start to interact with the water molecules in the triple NaCl-1W rings. In the most stable isomer of $NaCl^-(H_2O)_5$ (5A), the fifth H_2O forms hydrogen bonds with the water molecules in the NaCl-1W rings and the H_2O at the opposite side of Cl. In the second isomer of $NaCl^-(H_2O)_5$ (5B), only two NaCl-1W rings exist because the fifth H_2O breaks one NaCl-1W ring. Isomers 5A−5D are nearly degenerate in energy within a narrow energy range of 0.02 eV. The most stable isomer of $NaCl^-(H_2O)_6$ (6A) has two NaCl-1W rings because the fifth and sixth water molecules insert between Cl and another water molecule. Isomers 6B−6D of $NaCl^-(H_2O)_6$ can also emerge from isomer 4A by adding the fifth and sixth water molecules to different positions. They are close to 6A in energy. The calculated VDEs of the most stable isomers of $NaCl^-(H_2O)_5$ and $NaCl^-(H_2O)_6$ are in good agreement with the experimental values.

The Na−Cl distance in $NaCl^-(H_2O)_n$ increases significantly to 4.249 Å at n = 2 and drops slightly to 3.907, 3.816, and 3.774 Å at n = 3, 4, and 5, respectively. The Na−Cl distance of the most stable isomers for n = 2−6 are all much larger than that of n = 1 (2.629 Å). Thus, the transition from CIP structure to SSIP structure starts at n = 2. The decrease of the Na−Cl distances at n = 3−5 is more likely due to the increase of the Coulomb attraction between Na and Cl by delocalization of excess electron away from Na atom toward the water molecules. As can be seen from Figure 3, the singly occupied molecular orbitals (SOMOs) of the most stable structures of $NaCl^-(H_2O)_n$ shift away from the Na atom with increasing number of water moelcules especially at n = 3−6; thus, the Na atom shares less of the execss electron with increasing n. The natural population charge distributions of these clusters also confirmed this result (Figure S4).

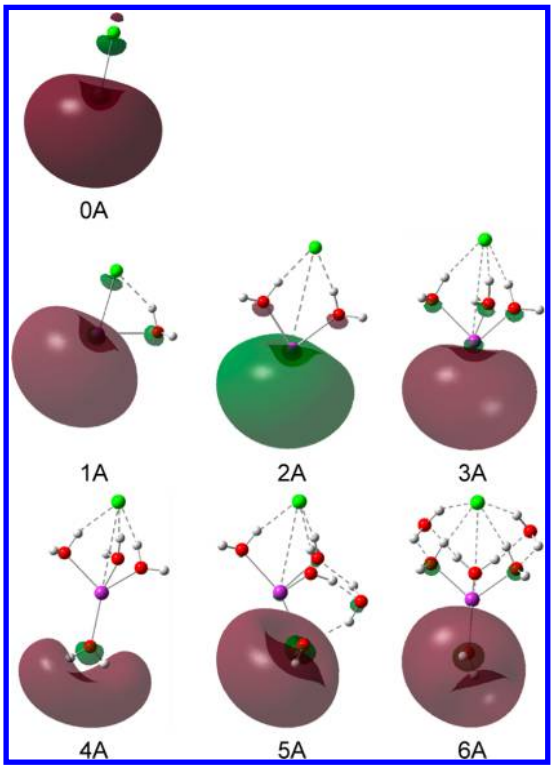

Figure 3. Diagrams of the singly occupied molecular orbitals (SOMOs) of the most stable structures of $NaCl^-(H_2O)_n$ (n = 0−6) (isovalue = 0.023).

Good agreement between the experimental and theoretical results for $NaCl^-(H_2O)_{1-6}$ anions confirmed the reliability of the theoretical methods. Here, we extend the theoretical calculations to neutral $NaCl(H_2O)_n$ clusters with n = 0−10 and 12. The structures of the neutral $NaCl(H_2O)_n$ clusters with n = 1−6 are shown in Figure 4, and those of n = 7−10 and 12 are displayed in Figure 5. Note that the structures of $NaCl(H_2O)_{11}$ are not investigated here because the structure optimization at the LC-ωPBE level already found that the SSIP structures of $NaCl(H_2O)_n$ are lower in energy than the CIP structures at n = 10 and 12. It is expected that the case of n = 11 is similar to those of n = 10 and 12.

The Na−Cl bond length of NaCl neutral is calculated to be 2.372 Å, in agreement with the value of 2.361 Å from microwave spectroscopy.[62] The most stable structures of neutral $NaCl(H_2O)$, $NaCl(H_2O)_2$, and $NaCl(H_2O)_3$ are characterized by the existence of NaCl-1W rings, as also shown by previous theoretical calculations[23,26] and FTMW spectroscopy study.[45] The second isomer of $NaCl(H_2O)$ (1B′), higher in energy than 1A′ by 0.228 eV, has a water molecule interacting with the Na atom through its O atom. NaCl-2W rings can also be formed in the other isomers of $NaCl(H_2O)_2$ (2B′) and $NaCl(H_2O)_3$ (3B′ and 3C′), but those isomers are higher in energy than the most stable ones by at least 0.06 eV.

The most stable isomer of $NaCl(H_2O)_4$ has two NaCl-1W rings and one NaCl-2W ring; that of $NaCl(H_2O)_5$ has one NaCl-1W ring and two NaCl-2W rings, while that of $NaCl(H_2O)_6$ is composed of three NaCl-2W rings. Starting at n = 7, $NaCl(H_2O)_6$ cuboidal unit (NaCl-6W cuboid) shows up, in which a Na atom, a Cl atom, and six H_2O molecules form a cuboid, with the Na atom interacting with the O atoms of nearby water molecules and the Cl atom forming hydrogen bonds with its neighboring water molecules. The most stable

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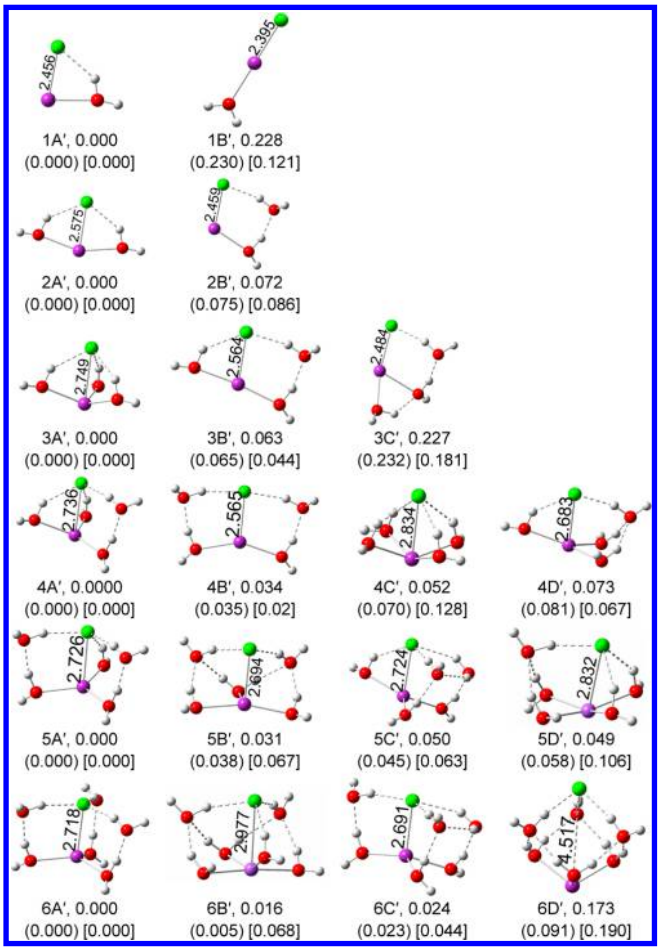

Figure 4. Typical low-lying isomers of $NaCl(H_2O)_n$ (n = 1−6). The relative energies (in electronvolts) of $NaCl(H_2O)_{1-4}$ were calculated at the CCSD(T)/aug-cc-pVTZ level of theory, and those of $NaCl(H_2O)_{5-6}$ were calculated at the CCSD(T)/maug-cc-pVTZ level of theory. The relative energies at the MP2/aug-cc-pVTZ and LC-ωPBE/6-311++G(d,p) levels are shown in the parentheses and brackets, respectively. The geometries were optimized at the LC-ωPBE/6-311++g(d,p) level of theory. All energies have been corrected by ZPEs obtained at the LC-ωPBE/6-311++g(d,p) level.

structure of $NaCl(H_2O)_7$ has a NaCl-6W cuboid and a NaCl-1W ring, and that of $NaCl(H_2O)_8$ has a NaCl-6W cuboid and a NaCl-2W ring. The most stable isomer of $NaCl(H_2O)_9$ has a distorted NaCl-6W cuboid and a NaCl-2W ring, and the ninth water molecule interacts with a Na−water edge of the cuboid and hence elongates that edge. The most stable isomer of $NaCl(H_2O)_{10}$ can be considered as consisting of a pair of coface NaCl-6W cuboids, and that of $NaCl(H_2O)_{12}$ is composed of a pair of coedge NaCl-6W cuboids. The most stable SSIP structure of $NaCl(H_2O)_{10}$ (10B′) (in which the Na^+ and Cl^- are separated by two layers of water molecules) is nearly degenerate with the CIP structure (10A′) in energy. It is higher in energy than 10A′ by only 0.002 eV at the CCSD(T) level. It seems that the formation of NaCl-6W cuboids can stabilize the CIP structure of $NaCl(H_2O)_{12}$ (12A′) and makes it lower in energy than the most stable SSIP structure (12B′) by 0.042 eV, indicating that the relative energy between the SSIP and CIP structures is not only size-dependent but also geometry-dependent.

The Na−Cl distances in neutral $NaCl(H_2O)_n$ are shorter than those in their anionic counterparts because the Na^+−Cl^- attraction in the neutral clusters is much stronger than that in the anions. The Na−Cl distances in the CIP structures of $NaCl(H_2O)_n$ increase from 2.46 to 2.88 Å with the increasing of n from 1 to 12. These values are close to the calculated Na−Cl distance of the CIP state (2.8 Å) in aqueous solutions.[34] The Na−Cl distances of the SSIP structures of $NaCl(H_2O)_{10}$ and $NaCl(H_2O)_{12}$ are 4.91 and 5.19 Å, respectively, also in agreement with the calculated Na−Cl distance of the SSIP state (5.0 Å) in aqueous solutions.[34,38,41]

For n = 1−6, the low-lying isomers of $NaCl(H_2O)_n$ clusters are dominated by CIP structures. The lowest SSIP structure of $NaCl(H_2O)_6$ (6D′) is higher in energy than the lowest CIP structure by 0.173 eV at the CCSD(T) level of theory. For n = 7 and 8, the lowest SSIP structures are higher in energy than the lowest CIP structures by 0.121 and 0.112 eV, respectively. At n = 9, 10, and 12, the CIP and SSIP structures are nearly degenerate in energy, with the SSIP structures being slightly higher in energy than the CIP structures by 0.017, 0.002, and 0.042 eV, respectively, at the CSSD(T) level of theory, all less than 1.0 kcal/mol. It is worth mentioning that the calculations at LC-ωPBE and MP2 levels suggest that the SSIP structure of $NaCl(H_2O)_{10}$ (10B′) is lower in energy than the CIP structure (10A′). Also, the calculations at LC-ωPBE level suggest the SSIP structure of $NaCl(H_2O)_{12}$ (12D′) to be the most stable one, while the calculations at the MP2 level imply that the SSIP structure of $NaCl(H_2O)_{12}$ (12B′) is nearly degenerate in energy with the most stable CIP structure (12A′). These facts indicate that the CIP−SSIP transition starts in the range of n = 9−12 except that the geometric factor contributes to the stabilization of the CIP structure at n = 12. It is worth mentioning that the second, third, and fourth isomers of $NaCl(H_2O)_{12}$ (12B′, 12C′, and 12D′) are all SSIP structures, suggesting that $NaCl(H_2O)_{12}$ prefers to form SSIP structures when the geometric factor does not take control.

In saturated aqueous NaCl solution (~6.16 M) at room temperature, on average about 9 water molecules are needed to dissolve a NaCl molecule. The degeneracy of the CIP and SSIP structures at n = 9−12 is somewhat coincident to the H_2O:NaCl molar ratio of the saturated solution. On the other hand, by considering the Boltzmann factors between the first two isomers, the SSIP−CIP ratios at n = 9, 10, and 12 are 52%, 93%, and 20%, respectively, at 300 K, indicating that the SSIP and CIP structures can coexist at room temperature. From the results of $NaCl(H_2O)_n$ clusters, one may infer that it is highly possible for both CIP and SSIP structures to be present in concentrated aqueous NaCl solutions. In fact, the X-ray diffraction experiments on saturated aqueous NaCl solutions[42] suggested that about 30% of the ions form Na^+−Cl^- CIPs with an averaged Na−Cl distance of 2.82(17) Å. The coherent results of the gas phase NaCl−water clusters and condensed phase solutions demonstrate that exploring the structures and properties of salt−water clusters can indeed provide valuable information for understanding the properties of aqueous salt solutions.

In summary, the structures of $NaCl(H_2O)_n$ clusters are charactrized by NaCl-1W and NaCl-2W rings at small size and by NaCl-6W cuboids at larger size. For the $NaCl^-(H_2O)_n$ anions, the transition from CIP structure to SSIP structure occurs at n = 2. Shift of the excess electron from Na toward water molecules can induce a slight decrease of Na−Cl distance in $NaCl^-(H_2O)_n$ anions. For neutral $NaCl(H_2O)_n$ of n = 1−8, the low-lying isomers of $NaCl(H_2O)_n$ clusters are dominated by CIP structures. At n = 9−12, the CIP structures and SSIP

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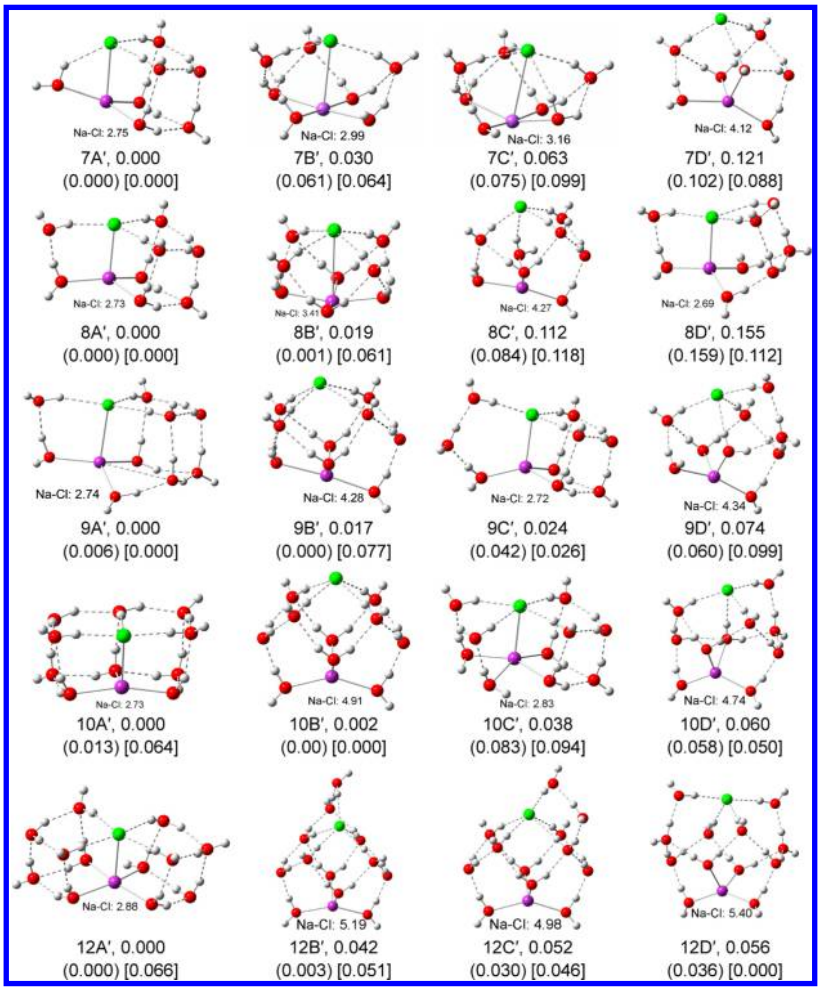

Figure 5. Typical low-lying isomers of $NaCl(H_2O)_n$ (n = 7−10, 12). The relative energies (in electronvolts) from different methods are shown in the order of CCSD(T)/maug-cc-pVTZ (MP2/aug-cc-pVTZ) [LC-ωPBE/6-311++G(d,p)]. The geometries were optimized at the LC-ωPBE/6-311++g(d,p) level of theory. All energies have been corrected by ZPEs obtained at the LC-ωPBE/6-311++g(d,p) level.

structures of $NaCl(H_2O)_n$ are almost degenerate in energy, indicating the CIP and SSIP structures can coexist in concentrated solutions. The degeneracy of the CIP and SSIP structures at n = 9−12 is coincident to the H_2O:NaCl molar ratio of the saturated solution. The coedge NaCl-6W cuboids CIP structure of $NaCl(H_2O)_{12}$ is slightly lower in energy than the most stable SSIP structure, indicating that geometry is also one of the important factors affecting the relative energies between CIP and SSIP structures. On the whole, $NaCl(H_2O)_{12}$ prefers to form SSIP structures when the geometric factor does not take control.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b02670.

Experimental and theoretical methods, details of molecular dynamics simulations, the 532 nm photoelectron spectra of $NaCl^-(H_2O)$ at different experimental conditions, simulated infrared spectra of the most stable structures of $NaCl(H_2O)_n$ (n = 1−6) neutrals, natural population charge distributions of the most stable structures of $NaCl^-(H_2O)_n$ (n = 0−6) anions, complete list of the low-lying structures of $NaCl^-(H_2O)_n$ anions and neutrals, as well as the MD population analyses of the CIP and SSIP structures for $NaCl(H_2O)_n$ (n = 8, 9, 10, and 12) clusters at different temperatures (PDF)

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Notes

The authors declare no competing financial interest.

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