

Communication: Infrared spectroscopy of salt-water complexes

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Communication: Infrared spectroscopy of salt-water complexes

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To explore how the ion-pair in a single salt molecule evolves with the addition of water, infrared (IR) spectra of complexes composed of NaCl and multiple water molecules have been recorded for the first time. The $\text{NaCl}(\text{H}_2\text{O})_n$ complexes were formed and probed in liquid helium nanodroplets, and IR spectra were recorded for $n = 1 \rightarrow 4$. The spectra for $n = 1, 2$, and 3 are consistent with formation of the lowest energy contact-ion pair structures in which each water molecule forms a single ionic hydrogen bond to an intact Na^+Cl^- ion-pair. Alternative structures with hydrogen bonding between water molecules become energetically competitive for $n = 4$, and the IR spectrum indicates likely the coexistence of at least two isomers. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4945342>]

The behaviour of ions is central to aqueous chemistry.^{1–3} In highly dilute solutions, cations and anions can be regarded as separate and non-interacting entities. However, in concentrated solutions, this assumption may no longer be valid and therefore a challenge in aqueous ion chemistry is to understand the extent and the impact of ion-pairing. Information about ion-pairs deduced from measurements of the properties of bulk solutions cannot directly reveal behaviour at the molecular scale. Consequently, recourse to simulations, such as those provided by molecular dynamics or Monte Carlo calculations, may provide valuable complementary information. Unfortunately, an accurate simulation of the properties of even simple electrolytic solutions is still an aspiration.⁴ One obstacle is finding a model potential that can satisfactorily account for both ion-solvent and ion-pair interactions.

One way of viewing ion-pairing is through the lens of the Eigen-Tamm model of ion association.⁵ Strong electrolytes at high dilution yield solutions where essentially all ions are fully separated and surrounded by water. However, ions in more concentrated solutions can associate to form contact ion-pairs (CIPs), solvent-separated ion-pairs (SIPs), and doubly solvent-separated ions pairs (2SIPs). These ion-pair states are considered to be distinct structures in equilibrium in solutions. Although evidence for these states is plentiful, direct experimental observation in bulk solutions is rare.⁶ An alternative means of gaining insight into ion-pairs is to “dissolve” a single molecule of the solute in a small water cluster. Such an approach has recently been used to explore the $\text{HCl}/\text{H}_2\text{O}$ system by spectroscopic observation of $\text{HCl}(\text{H}_2\text{O})_n$ complexes.^{7–11} With this method, it becomes possible to determine how the ion-pair evolves as the hydration number is changed. Indeed, with sufficient water molecules, the ions should separate into a SIP complex.

The focus here is on one of the most fundamental electrolytic systems, common salt (NaCl) in water. Although *ab initio* calculations on small $\text{NaCl}(\text{H}_2\text{O})_n$ complexes have been reported in several publications,^{12–17} there is a notable lack of experimental information to test these predictions. The first spectroscopic study of the simplest complex, $\text{NaCl}(\text{H}_2\text{O})$, used co-deposition of NaCl and water into an argon matrix.¹⁸ Infrared (IR) spectra revealed peaks in the OH stretching region which were assigned to $\text{NaCl}(\text{H}_2\text{O})$. Since that early work, the only other spectroscopic study of $\text{NaCl}(\text{H}_2\text{O})_n$ complexes was by Endo and co-workers, who obtained microwave spectra for $n = 1–3$.^{19,20} These were challenging experiments which have established the structures of the complexes in the gas phase. Analysis of the spectra was consistent with a CIP-like complex with the steady elongation of the Na–Cl bond as water molecules are added. However, the solvent stabilization provided by three water molecules is insufficient for a water molecule to squeeze between the Na^+ and Cl^- ions. Several theoretical predictions have suggested that this SIP formation becomes energetically viable at $n = 6$.^{14–16}

A major challenge in the experimental study of salt-water complexes is to find techniques for making these complexes and for recording their spectra. Ideally, the chosen method will be capable of accessing the various types of ion-pair complexes identified above. IR spectroscopy is a good option for recording spectra, since the OH stretching region is a sensitive probe of hydrogen bonding networks.

We address this challenge here by preparing salt-water complexes in liquid helium nanodroplets. These droplets are now an established means of isolating molecules and molecular complexes in a gas-like environment at low temperature (0.4 K).²¹ The helium nanodroplets were passed through two pick-up zones, the first containing NaCl vapor and the second water vapor. Figure 1 shows a mass spectrum recorded following electron ionization of the doped helium droplets. Two ion series are highlighted in this mass spectrum,

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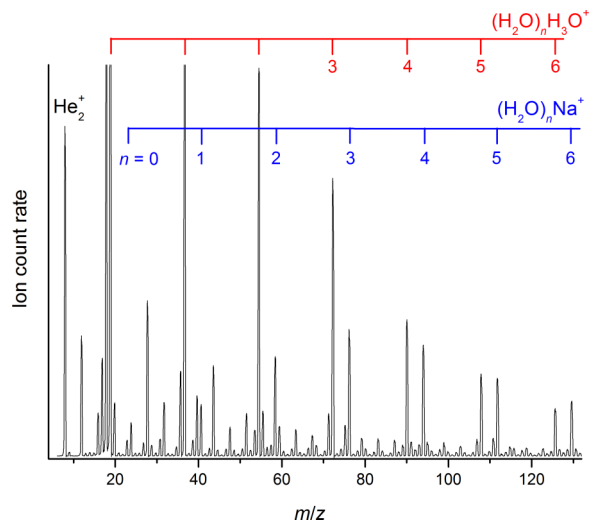


FIG. 1. Electron ionization mass spectrum from helium droplets doped with NaCl and H₂O molecules.

one from H₃O⁺(H₂O)_n and the other from Na⁺(H₂O)_n. Evaporation of NaCl at the temperature used (445 °C) produces NaCl molecules almost exclusively in the vapor, with negligible production of atomic sodium.²² Consequently, the Na⁺(H₂O)_n ions must come from ionization of NaCl(H₂O)_p in helium nanodroplets, where $p \geq n$ and the Cl atom is ejected from the ion (with or without the loss of water molecules) prior to detection.

IR spectra of the neutral complexes were recorded in the O–H stretching region using laser excitation. The binding energy of each helium atom to the droplet is 5 cm^{−1} and so the absorption of a photon at 3000 cm^{−1} and subsequent dissipation of that energy into the droplet will result in the loss of 600 helium atoms.²¹ Since the initial mean droplet size was on the order of 5000 helium atoms, the evaporation process presents a significantly smaller droplet into the electron ionization source with a reduced ionization cross section. Consequently, resonant absorption, which takes place prior to electron ionization of the doped droplet, could be registered via a decrease in the ion production rate. In this work, we chose to monitor Na⁺(H₂O)_n ions, since this confers a degree of mass selectivity to the IR spectra and should remove the strong absorption bands from pure water clusters.

Figure 2 shows IR spectra recorded by monitoring ions at m/z 23, 41, 59, and 77, which correspond to Na⁺, Na⁺(H₂O), Na⁺(H₂O)₂, and Na⁺(H₂O)₃, respectively. The number of water molecules in the chosen ion establishes the *minimum* number of water molecules in the corresponding neutral complex. The spectrum at m/z 23 in Figure 2(a) is unique in that it shows bands above 3300 cm^{−1} from water clusters up to and including the pentamer, (H₂O)₅. These bands remain when the salt oven is switched off, showing that they have no relationship to NaCl. Since the same water cluster spectrum can be recorded by detecting H₃O⁺, we assume that the water features seen in Figure 2(a) arise from small quantities of the He–H₃O⁺ formed on ionization. When the oven is switched on, we see two additional, and much sharper, peaks at 3150 and 3216 cm^{−1}. These two peaks also depend on the amount of water vapor and so are assigned to NaCl(H₂O)_n. To

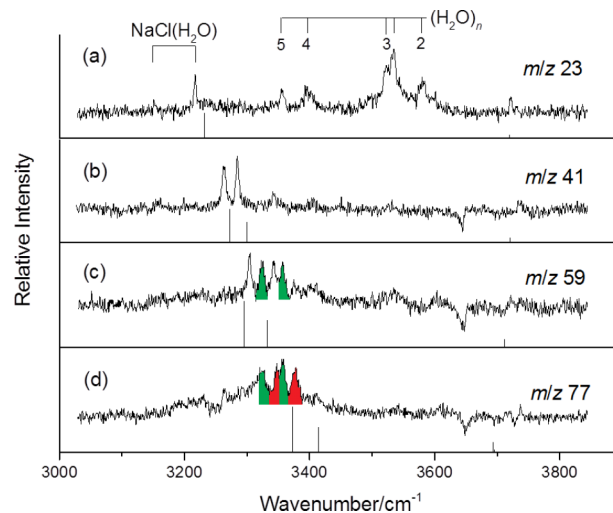


FIG. 2. Infrared depletion spectra recorded by detecting (a) Na⁺ (m/z 23), (b) Na⁺(H₂O) (m/z 41), (c) Na⁺(H₂O)₂ (m/z 59), and (d) Na⁺(H₂O)₃ (m/z 77). Stick spectra from MP2 calculations of the lowest energy isomers of NaCl(H₂O)_n for $n = 1$ –3 are also shown in (a)–(c). The theoretical spectrum in the bottom panel of (d) is for the highest energy (C_{4v}) isomer of NaCl(H₂O)₄. The peaks shaded red in (d) are assigned to this isomer while the green peaks in (c) and (d) are attributed to an unknown isomer of NaCl(H₂O)₄.

help in determining the value of n in this and other spectra, the dependence of the IR signal on the water pick-up cell pressure (PUCP) has been measured and the detailed findings are presented in the supplementary material.²³ The peaks at 3150 and 3216 cm^{−1} are both consistent with an assignment to NaCl(H₂O). The observation of this binary complex by detecting bare Na⁺ ions shows that the neutral complex loses both the Cl atom and a water molecule in the ionization process.

In support of the experiments, *ab initio* calculations were performed using MP2/aug-cc-pVTZ methodology and the principal findings are broadly in agreement with previous theoretical studies of NaCl(H₂O)_n.^{12–17} For $n = 1$ –4, only contact ion-pair structures are found in which there is a modest elongation in the Na–Cl distance as water molecules are added. Two distinct equilibrium structures were calculated for NaCl(H₂O). The global energy minimum, which is shown in Figure 3, has two OH environments, one corresponding to a dangling O–H bond and the other, which we denote as OH_b, locked into an ionic hydrogen bond (IHB) to the chloride ion. The IHB weakens the OH_b bond and so the OH_b stretching frequency is predicted to be strongly red-shifted relative to that of the “free” OH. Furthermore, a much larger transition dipole moment is expected for the bonded OH than the free OH because of the strong electrostatic polarization induced by the proximity of the former to Cl[−]. These predictions are reflected in the calculated spectrum for NaCl(H₂O) in Figure 2(a), which was derived from the harmonic oscillator approximation in combination with a scaling factor (see the supplementary material²³). The NaCl(H₂O) band at 3216 cm^{−1} is fairly close to the predicted band at 3232 cm^{−1}.

The much weaker band at 3150 cm^{−1} is not accounted for by the harmonic oscillator model and probably derives from the first overtone transition of the water bending vibration ($2\nu_2$), which is calculated to be near 3100 cm^{−1}. This

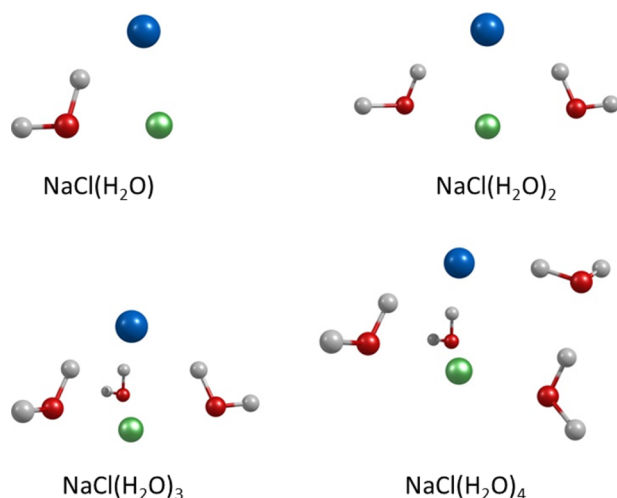


FIG. 3. Lowest energy structures of $\text{NaCl}(\text{H}_2\text{O})_n$ from MP2 calculations for $n = 1-4$. The full set of calculated equilibrium structures is provided in the supplementary material.²³

overtone may gain some intensity through Fermi resonance given its proximity to the OH_b stretching transition. An equivalent Fermi resonance interaction has been identified in the $\text{Cl}^-(\text{H}_2\text{O})$ anion, where the Cl^- forms an IHB to the water molecule.²⁴ The interaction matrix element in that case was determined to be close to 30 cm^{-1} . From the positions and relative intensities of the $\text{NaCl}(\text{H}_2\text{O})$ bands, we deduce a matrix element of $\sim 27 \text{ cm}^{-1}$,²³ which is similar to that determined for $\text{Cl}^-(\text{H}_2\text{O})$ and which therefore supports the current $\text{NaCl}(\text{H}_2\text{O})$ band assignments.

As anticipated by the calculations, the OH_b stretching frequency is red-shifted by ca. 500 cm^{-1} relative to the OH stretches of H_2O . For $\text{Cl}^-(\text{H}_2\text{O})$, the OH_b band was found at 3146 cm^{-1} ,²⁵ 70 cm^{-1} to the red of that for $\text{NaCl}(\text{H}_2\text{O})$. A larger red-shift for $\text{Cl}^-(\text{H}_2\text{O})$ is reasonable because the bonded OH is exposed to the full negative charge on the chloride ion, whereas a smaller partial charge is expected on the chloride ion in $\text{NaCl}(\text{H}_2\text{O})$. Nevertheless, the modest difference in the OH_b stretching frequencies of $\text{Cl}^-(\text{H}_2\text{O})$ and $\text{NaCl}(\text{H}_2\text{O})$ is consistent with the strongly ionic character of NaCl.

In the only previously reported IR study of $\text{NaCl}(\text{H}_2\text{O})$, carried out in an argon matrix, bands at 3141 and 3251 cm^{-1} were assigned to this complex.¹⁸ These bands are reasonably close to those observed in our work if we allow for a red-shift of $20\text{--}30 \text{ cm}^{-1}$, which is certainly possible.²⁶ Note also that the higher frequency band in the matrix experiment is much stronger than the lower frequency band, which again agrees with our findings. However, the matrix IR spectrum was assigned to the other isomer of $\text{NaCl}(\text{H}_2\text{O})$, which we calculate to be 0.23 eV above the global minimum. This has a C_{2v} structure in which the Na^+ locates itself between the Cl^- and the O atoms. This assignment is incorrect, because the two OH stretching bands of the C_{2v} structure of $\text{NaCl}(\text{H}_2\text{O})$ must fall in the free OH stretching region near to 3700 cm^{-1} , as our MP2 calculations show. Furthermore, since we do not see these two distinct bands in our spectrum in Figure 2(a), we conclude that the C_{2v} structure is not significant in helium droplets.

Turning to larger complexes, we see two bands of nearly equal intensity in the OH_b part of the IR spectrum when monitoring $\text{Na}^+(\text{H}_2\text{O})$. This simple spectrum, shown in Figure 2(b), is in good agreement with that predicted from the *ab initio* calculations for the lowest energy isomer of $\text{NaCl}(\text{H}_2\text{O})_2$. Like $\text{NaCl}(\text{H}_2\text{O})$, the calculations show that the Na^+Cl^- ion pair remains intact and the two prominent OH stretching bands derive from symmetric and antisymmetric combinations of the two OH_b stretches. The MP2 calculations predict a splitting of 28 cm^{-1} between these two bands, which is fairly close to the experimental band separation of 21 cm^{-1} . Furthermore, the theory predicts that the OH_b bands of $\text{NaCl}(\text{H}_2\text{O})_2$ are blue-shifted relative to that of $\text{NaCl}(\text{H}_2\text{O})$, which is also in agreement with our experiment. Since all contributions from pure water clusters are removed from this spectrum, we can see a weak free OH stretching band at 3734 cm^{-1} , which is assigned to $\text{NaCl}(\text{H}_2\text{O})_2$. As was the case with $\text{NaCl}(\text{H}_2\text{O})$, it is clear from the IR assignments that ionization of $\text{NaCl}(\text{H}_2\text{O})_2$ leads to ejection of both a Cl atom and a water molecule and so by detecting $\text{Na}^+(\text{H}_2\text{O})$, we get a relatively clean IR spectrum of $\text{NaCl}(\text{H}_2\text{O})_2$.

The spectroscopy becomes more complicated for larger $\text{NaCl}(\text{H}_2\text{O})_n$ complexes. The spectrum in Figure 2(c) was obtained by detecting $\text{Na}^+(\text{H}_2\text{O})_2$. Four pronounced bands at 3305 , 3321 , 3341 , and 3357 cm^{-1} are seen in the OH_b stretching region, whereas only two are expected from the global minimum in Figure 3 (two of the OH_b stretching vibrations are degenerate). The PUCP data for the two bands at 3305 and 3341 cm^{-1} are consistent with an assignment to $\text{NaCl}(\text{H}_2\text{O})_3$.²³ In support of this assignment, the separation between these two peaks is almost identical to that predicted by the MP2 calculation.

The PUCP data for the other two peaks in Figure 2(c), marked in green and located at 3321 and 3357 cm^{-1} , suggest that they derive from $\text{NaCl}(\text{H}_2\text{O})_4$. MP2 calculations support this assignment since all isomers of $\text{NaCl}(\text{H}_2\text{O})_3$, apart from the global minimum, predict at least one intense IR band at $\leq 3150 \text{ cm}^{-1}$, and no such band is observed.

In Figure 2(d), there are at least four distinct peaks with substantial intensities in the OH_b region of Figure 2(d), as well as several weaker peaks. A broad and almost continuous underlying absorption spanning $3150\text{--}3400 \text{ cm}^{-1}$ is also evident. The strongest bands are attributed to two isomers of $\text{NaCl}(\text{H}_2\text{O})_4$, one of which is a structure with C_{4v} symmetry in which all four water molecules are bound to the chloride ion via ionic hydrogen bonds. Steric effects mean that this structure is not the global minimum for $\text{NaCl}(\text{H}_2\text{O})_4$. The peaks assigned to this isomer are marked in red in Figure 2(d) and show a similar separation to the MP2 predictions for this isomer in the bottom panel. The other two strong peaks in Fig. 2(d) are shaded green and coincide with the green peaks identified in Fig. 2(c). It seems likely that these peaks in both spectra come from the same complex and we assign these to a different isomer of $\text{NaCl}(\text{H}_2\text{O})_4$, although there is no good fit to the MP2 spectra of any of the other isomers of $\text{NaCl}(\text{H}_2\text{O})_4$ that we have found (see supplementary material²³). This assignment is therefore tentative and we cannot rule out contributions from $\text{NaCl}(\text{H}_2\text{O})_5$ and larger complexes. Certainly more systematic and detailed searches

of the potential energy landscape of $\text{NaCl}(\text{H}_2\text{O})_4$ would be welcome.

To summarize, the first infrared spectra of $\text{NaCl}(\text{H}_2\text{O})_n$ have been reported for a range of n . IR bands for $n = 1$ -3 have been firmly assigned and all arise from the global potential energy minimum in each case. The water molecules in these contact ion-pair complexes bind to Cl^- via ionic hydrogen bonds. Bands are also seen from $\text{NaCl}(\text{H}_2\text{O})_4$ but these are difficult to assign for several reasons, including likely contributions from multiple isomers. These findings illustrate some of the strengths and challenges in using helium droplets to explore complexes between solvent and salt molecules. A study of the interaction of a variety of salt molecules with water, and indeed other solvents, should be straightforward. However, the complexity seen in the spectroscopy of $\text{NaCl}(\text{H}_2\text{O})_n$ for $n \geq 4$ suggests that it will be difficult to obtain definitive spectroscopic evidence for solvent-separated ion-pair structures.

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²³See supplementary material at <http://dx.doi.org/10.1063/1.4945342> for more details about the experimental methodology and calculations.

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