

Microscopic Hydration of the Sodium Chloride Ion Pair

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Hydration of ion pairs is an essential process in the solvation of ionic crystals into water,¹ chemical reactions in aqueous solution,² and stability and functionality of biological systems.³ Since Winstein et al.⁴ proposed a contact ion pair (CIP) and a solvent-separated ion pair (SSIP) as intermediates in solution, the microscopic nature of the ion pairs has been the subject of numerous studies. Especially, because of its familiarity and simplicity, sodium chloride (NaCl) has been examined most extensively by diffraction⁵ and NMR⁶ experiments and by theory using integral equations⁷ and computer simulations.⁸

Interactions involved in the hydration of sodium chloride can be evaluated in detail by studies of NaCl-(H₂O)_n clusters, to which theory has mostly contributed at present.^{9–14} Several isomeric forms have been identified, and their relative stability is sensitive to the level of calculations or adopted empirical potentials. The highest level ab initio calculations¹⁰ yet performed predicted that each water molecule makes close contact with both ions to form a four-membered ring at the global minimum (Figure 1). The only experimental study, which reported the infrared spectrum of matrix-isolated NaCl-H₂O,¹³ provided no definitive information on the cluster structure, because the spectrum could not be reproduced as any isomeric form predicted so far,^{9,10} probably because of significant matrix shifts in the observed frequencies.

Here we report the experimental characterization of NaCl solvated with a finite number of water molecules. We measured rotational spectra of NaCl-(H₂O)_n (*n* = 1–3) by using a Fourier transform microwave (FTMW) spectrometer coupled with a laser ablation nozzle source.^{15,16} The clusters were formed in an adiabatic expansion of laser-vaporized NaCl with an Ar stream containing a trace amount of water. More than 50 transitions were observed in 5–25 GHz, all of which show complicated hyperfine splitting originating from the nuclear quadrupole interactions due to the Na and Cl nuclei with ³/₂ spins. The observed lines have been assigned to two asymmetric tops (*n* = 1 and 2) and one symmetric top (*n* = 3) for both the Na³⁵Cl and the Na³⁷Cl isotopomers. The *n* = 2 cluster has been confirmed to be of C₂ symmetry on the basis of the observed intensity alternation and lack of a-type transitions. Spectra of two deuterated species, Na³⁵Cl-D_aH_bO and Na³⁵Cl-H_aD_bO, were also observed by using heavy water. (We hereafter call the in-ring H atom as H_a and the other as H_b.) Analyses with a rotational Hamiltonian including centrifugal distortion terms and hyperfine interactions have yielded the rotational constants, which are in close match with those predicted¹⁰ for the ring forms (Figure 1). They have been confirmed as the most stable isomers, because no other isomeric forms have been observed in the present experimental conditions with the rotational temperature of ~1 K. Quantum tunneling splitting due to permutation of bonded and

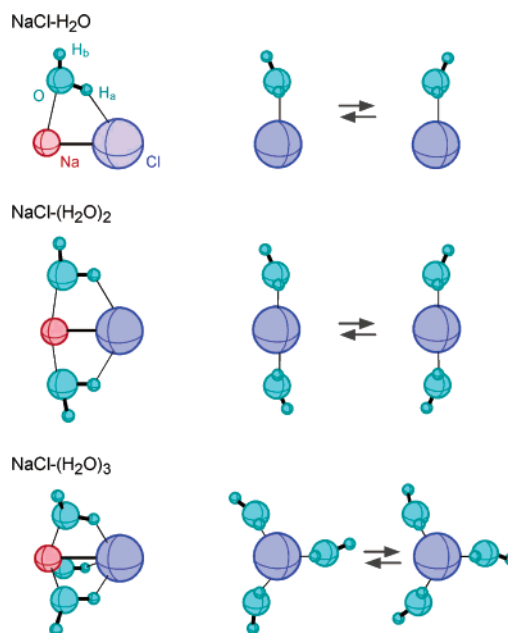


Figure 1. Structures of NaCl-(H₂O)_n derived theoretically and confirmed by the present experiments. Coordinates are from our CCSD(T)/6-311++G-(2d,2p) calculations using the MOLPRO package.¹⁷ MP2 calculations with cc-pVDZ and aug-cc-pVDZ basis sets¹⁰ give similar results. The barrier for the H_b flipping motion below and above the plane is predicted to be quite low (~0.04 kcal),¹⁰ making the interconversion between the right- and left-handed enantiomers feasible, as indicated in the side view (right). Because of this dynamical removal of chirality, the vibrationally averaged structures belong to C_s, C_{2v}, and C_{3v} symmetries for *n* = 1, 2, and 3, respectively.

nonbonded H atoms has not been observed for all of the transitions with the experimental resolution of ~10 kHz.

Experimentally determined rotational constants have been subjected to nonlinear least-squares regressions for the structure determination. Strong interactions between the Na⁺Cl⁻ ion pair and water molecules are clearly evident in the determined cluster structures. The *r*(Na-O) and *r*(Cl-H_a) distances in *n* = 1 are determined as 2.27 and 2.28 Å, respectively, much shorter than the sum of the ionic and vdW radii. The most striking observation is the substantial increase in the *r*(Na-Cl) distance with the successive addition of water. The distance in the *n* = 1 cluster is longer by 0.06 (2) Å than that of the free NaCl.¹⁸ The increments per one water addition for *n* = 2 and 3 become much larger, yielding the 0.48 (6) Å increase for *n* = 3 from free NaCl. The experimentally determined *r*(Na-Cl) distances are compared with the results from the ab initio calculations (Figure 2a). Changes by the microscopic hydration are well reproduced theoretically, although the calculations slightly underestimate the increments for *n* ≥ 1.

The microhydration effect on the Na⁺Cl⁻ ion pair is also apparent from substantial changes of the nuclear quadrupole coupling

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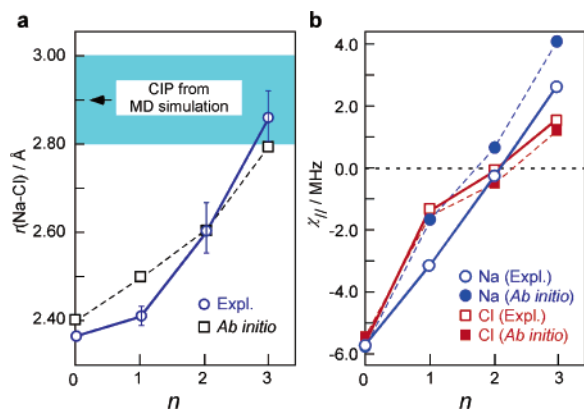


Figure 2. Molecular parameters in $\text{NaCl}-(\text{H}_2\text{O})_n$ versus the number of solvating waters, n . (a) The experimental values for the $r(\text{Na-Cl})$ bond distance plotted along with the theoretical results from our CCSD(T)/6-311++G(2d,2p) calculations. The distance in the CIP state in aqueous solution predicted by the molecular dynamics simulation^{8e} is also indicated. (b) The experimental χ constants for the Na and ³⁵Cl nuclei along the Na-Cl axis as compared to those from the MP2/6-311++G(2d,2p) calculations using the Gaussian 94 program.²¹ To derive the observed values for $n = 1$, calculated off-diagonal elements of the χ tensor are used after rescaling.

(commonly denoted as χ) constants determined from the analysis of the hyperfine splitting. Elements of the χ tensor are proportional to the electric field gradients at a nucleus, so they sensitively probe the charge distribution around it.¹⁹ The χ components along the Na-Cl axis have small negative values for both the Na and the Cl nuclei in free NaCl,²⁰ representing the small covalent-bond character in the ionic molecule.¹⁹ They gradually increase as the number of attached waters increases, finally being positive for $n = 3$ (Figure 2b). The changes indicate that the principal directions of the electron distribution in the atoms are rotated away from those in the free molecule because of polarization and/or charge transfer by the directly contacting O and H_a of waters. Such a charge rearrangement around Na and Cl will be the initial step toward the complete charge separation in the ion pair at the extended level of hydration. The present MP2/6-311++G(2d,2p) calculation shows that the electron density between Na⁺ and Cl⁻ is substantially reduced as n becomes larger in $\text{NaCl}-(\text{H}_2\text{O})_n$. This correlated level of theory using a moderately large basis set is sufficient to reproduce the gross feature of the charge rearrangement, as seen in the reasonable agreement between the calculated and observed χ constants.

The previous theoretical studies^{7,8} of NaCl in aqueous solution have revealed CIP and SSIP as two distinct minima in the potential of mean force, which expresses the free energy of the ion pair as a function of the ion separation. The first minimum corresponding to CIP has been located at ~ 2.9 Å. The position of the second (i.e., SSIP) minimum depends on the model potential, and the most sophisticated one^{8e} considering the polarizability of water located it at ~ 5.1 Å. The ion separation in CIP is substantially larger than that in the free NaCl molecule, even though the Na⁺ and Cl⁻ ions “directly” contact with each other in CIP. It is the consequence of the large modification on the electrostatic interaction between the ions by nearby waters in solution. The present experimental investigation has confirmed that such a modification is already operative in $\text{NaCl}-(\text{H}_2\text{O})_n$ ($n = 1-3$). Especially, the $r(\text{Na-Cl})$ distance for $n = 3$ reaches the value estimated for CIP. This implies considerable similarity between the local solvation structure in CIP and the clusters with small size.

In conclusion, solvation structure and internal dynamics of the hydrated ion pairs, $\text{NaCl}-(\text{H}_2\text{O})_n$ ($n = 1-3$), have been studied in detail by the measurement of their rotational spectra. The ion-pair structural transition from a free ionic-bond molecule to a hydrated CIP in finite system has been established as a pronounced increase in the Na⁺-Cl⁻ separation with an increasing degree of solvation. The present experimental results will be useful to refine the interaction models adopted in the molecular dynamics or Monte Carlo simulations for the microscopic description of the ion pair in solution.

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Supporting Information Available: Spectroscopic constants and structural parameters of the $\text{NaCl}-(\text{H}_2\text{O})_n$ clusters with $n = 1-3$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Ohtaki, H.; Yamatera, H., Eds. *Structure and Dynamics of Solutions*; Elsevier: Amsterdam, 1992.
- (a) Szwarc, M., Ed. *Ions and Ion Pairs in Organic Reactions*; Wiley: New York, 1974. (b) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1979.
- Conway, B. E. *Ionic Hydration in Chemistry and Biophysics*; Elsevier: Amsterdam, 1981.
- Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597-2598.
- (a) Pálincás, G.; Randi, T.; Hajdu, H. Z. *Z. Naturforsch.* **1980**, *A35*, 107-114. (b) Ohtomo, N.; Arakawa, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1789-1794. (c) Cummings, S.; et al. *Nature* **1980**, *287*, 714-716.
- Van der Maarel, J. R. C.; Lankhorst, D.; De Bleijser, J.; Leyte, J. C. *J. Phys. Chem.* **1986**, *90*, 1470-1478.
- (a) Patey, G. N.; Carnie, S. L. *J. Chem. Phys.* **1983**, *78*, 5183-5190. (b) Pettitt, B. M.; Rossky, P. J. *J. Chem. Phys.* **1986**, *84*, 5836-5844.
- (a) Berkowitz, M.; Karim, O. A.; McCammon, J. A.; Rossky, P. J. *J. Chem. Phys. Lett.* **1984**, *105*, 577-580. (b) Belch, A. C.; Berkowitz, M.; McCammon, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1755-1761. (c) Karim, O. A.; McCammon, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1762-1766. (d) Smith, D. E.; Haymet, A. D. J. *J. Chem. Phys.* **1992**, *96*, 8450-8459. (e) Smith, D. E.; Dang, L. X. *J. Chem. Phys.* **1994**, *100*, 3757-3766.
- Kulkarni, G. V.; Rao, C. N. R. *J. Mol. Struct.* **1983**, *100*, 531-537.
- Woon, D. E.; Dunning, T. H., Jr. *J. Am. Chem. Soc.* **1995**, *117*, 1090-1097.
- Asada, T.; Nishimoto, K. *Chem. Phys. Lett.* **1995**, *232*, 518-523.
- Petersen, C. P.; Gordon, M. S. *J. Phys. Chem. A* **1999**, *103*, 4162-4166.
- Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426-2433.
- Jungwirth, P. *J. Phys. Chem. A* **2000**, *104*, 145-148.
- (a) Suenram, R. D.; Lovas, F. J.; Matsumura, K. *Astrophys. J. Lett.* **1989**, *342*, L103-L105. (b) Suenram, R. D.; Lovas, F. J.; Fraser, G. T.; Matsumura, K. *J. Chem. Phys.* **1990**, *92*, 4724-4733.
- (a) Ohshima, Y.; Endo, Y. *Chem. Phys. Lett.* **1993**, *213*, 95-100. (b) Mizoguchi, A.; Endo, Y.; Ohshima, Y. *J. Chem. Phys.* **1998**, *109*, 10539-10542.
- MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, et al.
- Clouser, P. L.; Gordy, W. *Phys. Rev.* **1964**, *134A*, 864-870.
- Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; Dover: New York, 1975; Chapter 9.
- de Leeuw, F. H.; van Wachen, R.; Dymanus, A. *J. Chem. Phys.* **1970**, *53*, 981-984.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

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