

A Mechanism of the Ion Separation of the NaCl Microcrystal via the Association of Water Clusters

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The title heterolytic cleavage process of the NaCl microcrystal was studied by through ab initio calculations. First, a Na–Cl diatomic molecule was subjected to H₂O association. However, the heterolysis of Na⁺ and Cl[−] was not achieved even after adding eight water molecules. Second, two cluster models, (NaCl)_m(H₂O)_n (*m* = 4 and 6), were examined. At *n* = 6, an incipient dissociated model, where a pair of corner sodium and chloride ions leaves the NaCl cluster, was successfully obtained. When two lone-pair orbitals of a water molecule are directed toward the two sodium ions, the acidity of the hydrogen atoms of the H₂O molecule is enhanced, leading to a strong hydrogen bond with a chloride ion. The hydrogen-bond directionality compels the ion to leave the corner site. Thus, the heterolytic dissociation is initiated by the cooperative dissociation of two ions with the aid of polarized water molecules. The (NaCl)₄(H₂O)₉ model can describe a complete Na⁺ and Cl[−] dissociation.

I. Introduction

The dissolution of a salt, e.g., sodium chloride, is a fundamental phenomenon in chemistry. When an ionic crystal of NaCl is placed into water, the surface of the crystal becomes covered with water molecules. Sodium and chloride ions leave the surface of the crystal and disperse into the aqueous phase (Scheme 1).¹

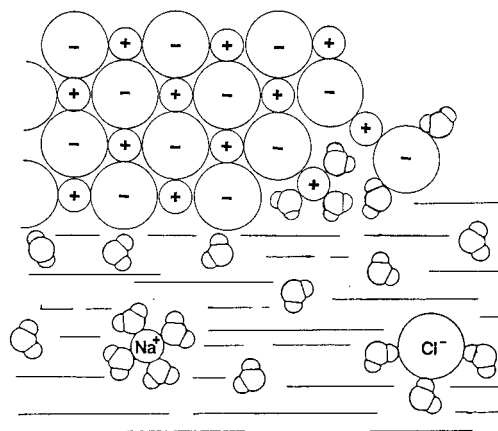
The dissolution process involves a “tug of war” between the ionic bonds and the hydration of those ions. Despite our familiarity with the phenomenon, the process is still microscopically unclear. It is a question of how the Na⁺ and Cl[−] ions are pulled out by the water molecules. Scheme 1 must include geometric conditions to elucidate the process correctly. In particular, two problems need to be solved:

(1) The binding energy of Na⁺⋯OH₂ is larger than that of Cl[−]⋯H–OH. Is the sodium ion pulled first from the surface of crystals?

(2) Do sodium and chloride ions leave the surface independently or cooperatively?

The dissolution process of a sodium chloride crystal in water was studied by molecular dynamics simulations.^{2–4} A chloride ion at a corner of the crystal was shown to dissolve first in water.^{2a} Repulsive forces between chloride ions and water molecules hydrating the sodium ions were suggested as the driving force for separating Cl[−] ions from the crystal.^{2b} It was also suggested that one of the protons in the hydrated water molecules tends to form a linear hydrogen bond with Cl.^{2b} In another study, the ion–water structure and bulk water properties were reproduced well in a polarizable water model for aqueous sodium chloride.³ Asada and Nishimoto suggested a scheme: water molecules are first hydrated with Na⁺ cations, and then, the water molecules are shared with a cation and an anion.⁴ There have been experimental⁵ and theoretical^{6–9} studies of interactions between NaCl microclusters and water molecules. Water molecules are bound to the diatomic NaCl molecule in a bridge form. The binding energies of NaCl⋯H₂O and NaCl(H₂O)⋯H₂O are ca. 17 kcal/mol.⁷ A water molecule is linked

SCHEME 1: Hydration of NaCl Ions for Electrolytic Dissociation in Aqueous Medium



with the Na ion of a cubic (NaCl)₄ cluster preferentially by the bridge form.⁹ The (NaCl)₄⋯OH₂ binding energy was calculated to be 11.3 kcal/mol.

For problem 1, chloride ions exit first despite the difference in binding energies, $\Delta E(\text{Na}^+\cdots\text{OH}_2) = 24.0 \text{ kcal/mol}^{10} > \Delta E(\text{Cl}^-\cdots\text{H}-\text{OH}) = 14.9 \text{ kcal/mol}^{11}$. For problem 2, the departure of Cl[−] and Na⁺ ions from the surface seems to be cooperative. A clearer insight into the initial process of the NaCl ion separation is needed.

In this work, the association of water molecules to NaCl, (NaCl)₄, and (NaCl)₆ clusters was studied through ab initio calculations to understand the dissolution mechanism. Interactions between the NaCl microclusters and water molecules were examined. The present calculations will rationalize the geometries in Scheme 1. In particular, it will be shown that the directionality of the hydrogen bonds is a primary driving force of the Cl[−] dissociation from NaCl clusters. It should be noted that the present calculations deal with potential surfaces of reactions which are of not dynamic but static character.

II. Method of Calculations

Ab initio calculations were performed using the GAUSSIAN 94 program.¹² The program was installed on the CONVEX SPP-1200/XA computer in the Information Processing Center (Nara University of Education). $(\text{NaCl})_m(\text{H}_2\text{O})_n$ clusters ($m = 1, 4$, and 6 ; $n = 1-9$) were investigated. Since these clusters are very large, RHF/3-21G was adopted first for the geometry optimizations. To assess the reliability of RHF/3-21G computed results, we carried out Becke3LYP/6-31(+)*G* calculations¹³ for some important systems, $(\text{NaCl})_1(\text{H}_2\text{O})_n$ ($n = 0-7$), $(\text{NaCl})_6(\text{H}_2\text{O})_n$ ($n = 0, 3$, and 6), and $(\text{NaCl})_4(\text{H}_2\text{O})_n$ ($n = 2, 4$, and 9). Here, 6-31(+)*G* denotes the 6-31G* basis set, augmented by an sp-type diffuse function¹⁴ on one selected chloride ion (Gaussian exponent = 0.0483). To obtain reliable binding energies ($-\Delta E$ s), we performed single-point calculations at the Becke3LYP/6-311+G(2d,p) level on RHF/3-21G geometries.

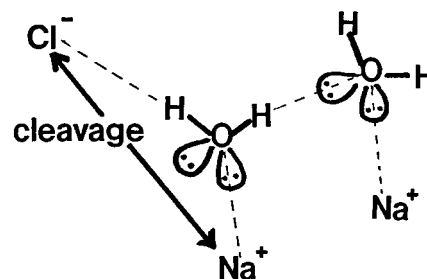
III. Results of Calculations and Discussions

As a first step in investigating the hydration of NaCl crystals, we considered a NaCl diatomic molecule surrounded by water molecules. Experimentally, the NaCl molecule generated at extremely high temperatures ($T = 1413^\circ\text{C}$) in the gas phase is usually unrealistic. However, in aqueous media, the molecule might be a unit of the dissolution. In fact, the geometries of $\text{NaCl}\cdot(\text{H}_2\text{O})_n$ ($n = 0-2$) aggregates have been investigated by highly accurate calculations.⁷ Figure 1 shows the geometries of $\text{NaCl}\cdots(\text{H}_2\text{O})_n$ ($n = 0-8$) aggregates, where isomeric structures with the geometry in $n = 1a$ are more stable than those with the geometry in $n = 1b$ (with the RHF/3-21G basis set).

The binding energy at the B3LYP/6-311+G(2d,p)//B3-LYP/6-31(+)*G* level of Na-Cl relative to that of Na^+ and Cl^- is 133.15 kcal/mol, which is comparable to the 130.53 or 121.31 kcal/mol from the local spin-density functional (LSD) or the post-LSD method, respectively.⁹ Those of $\text{Na}^+\cdots\text{OH}_2$ and $\text{Cl}^-\cdots\text{H}-\text{OH}$ are 24.59 (exptl 24.0¹⁰) kcal/mol and 14.2 (exptl 14.9¹¹) kcal/mol, respectively. Water molecules are linked preferentially with the sodium atom in the Na-Cl diatomic molecule. In $n = 1a$ in Figure 1, the predominant $\text{O}\cdots\text{Na}$ attraction and the neighboring $\text{O}-\text{H}\cdots\text{Cl}^-$ distorted hydrogen bond are shown. This coordination occurs also at $n = 2$ and 3 . At $n = 4a$, the Na-Cl distance is 3.06 [2.78] Å. Further H_2O coordination would be expected to bring about Na^+ and Cl^- dissociation. However, at $n > 4$, water molecules can no longer coordinate to both ions, and strong water-water interactions start developing. This leads to a shortening of the Na-Cl distance, increasing the number of water molecules. For instance, the distances are 2.74 [2.78] Å for $n = 6a$ and 2.77 Å for $n = 8a$. When the geometries in Figure 1 are considered, the Na-Cl diatomic molecule seems to not dissociate into Na^+ and Cl^- ions with any number of water molecules. It seems that the structures of the NaCl cluster surface and adjacent water layer play an important role in the dissociation process. The NaCl molecule, although not dissociated, polarizes H_2O molecules substantially. Binding energies ($-\Delta E$'s) are roughly in the range of strong hydrogen bonds.

Figure 2 exhibits the geometries of $(\text{NaCl})_6(\text{H}_2\text{O})_n$ ($n = 0-6$) aggregates. The $(\text{NaCl})_6$ model ($n = 0$) has step and corner ions ready for dissociation. The central square of the model has a Na-Cl distance of 2.82 [2.84] Å, which is close to that of the bulk crystal observed with an X-ray, 2.814 Å. When a water molecule is attached to the $(\text{NaCl})_6$ cluster, four isomeric structures of $n = 1$ are obtained. The best coordination is on the corner sodium ion in $n = 1a$. However, the $n = 1a$ model

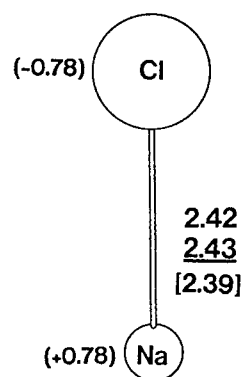
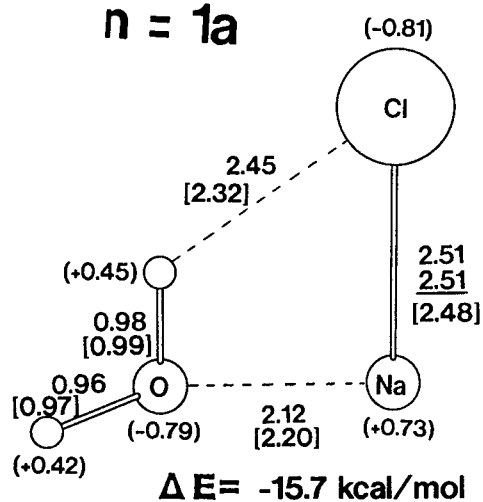
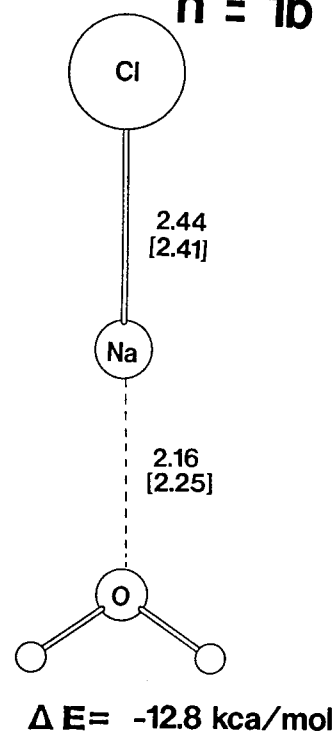
SCHEME 2: Driving Force for the Na^+-Cl^- Separation



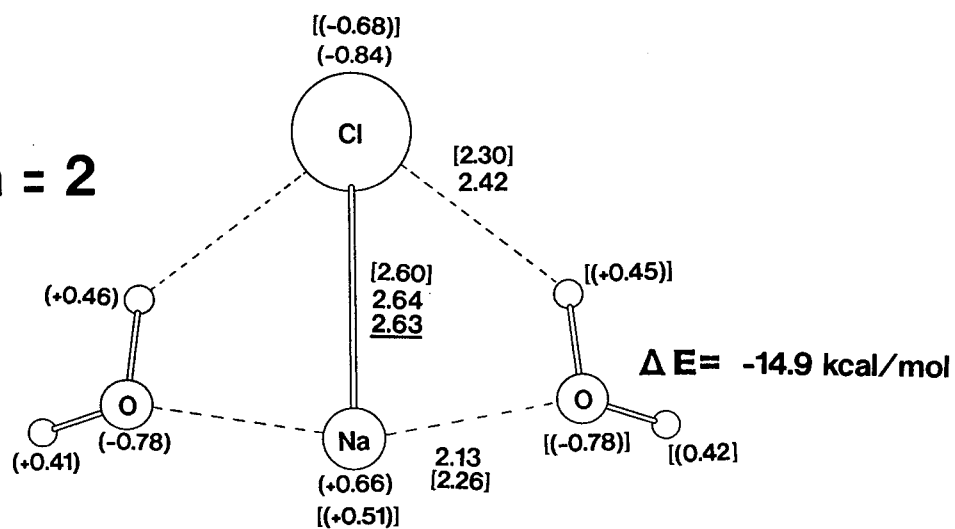
does not involve significant Na-Cl elongation. The $n = 1d$ model, with a Na-Cl distance of 3.03 Å, is noteworthy. The water molecule is coordinated to two sodium ions in a bridge form. Model 1d is instructive in that the operation of two lone-pair orbitals leads to the elongation of the Na-Cl bond. Next, two isomers of $n = 2$ are examined in Figure 2. The $n = 2a$ geometry has two Na-Cl bonds of 3.05 Å. The corner sodium ion is the target for hydration in $n = 2a$ and $2b$. Two isomers of $n = 3$ are examined. The addition of H_2O to $n = 2a$ does not lead to any significant geometric change for $n = 3a$. Simple H_2O coordination with the corner sodium atom does not seem to be a driving force for the ion separation. In this respect, the $n = 4$ models are informative. In $n = 4a$ in Figure 2, a Na-Cl bond is completely broken, in terms of distances, by a water dimer. Water molecules polarized by sodium ions form hydrogen bonds with chloride ions. The hydrogen-bond directionality brings about the Na-Cl dissociation (Scheme 2).

Next, the $n = 5$ geometries are examined. The $n = 5a$ model does not lead to effective ion separation, and a "molecular" NaCl is retained. It is not the number of H_2O molecules but their orientation which is thought to have a key role in the ion separation. When the geometry in Scheme 2 is followed, dissociation is obtained successfully at $n = 6$. Two ions are separated with three H_2O molecules intervening. Two of the three follow the geometry arrangement in Scheme 2 and are coordinated in the bridge form to two sodium ions. The chloride ion is pushed away by three water molecules which are polarized by sodium ions. Two ions leave the surface cooperatively. The Cl^- ion leaves the surface first, followed by the departure of the Na^+ ion. The Cl^- departure described by Ohtaki et al.² is explicable in Scheme 2. Figure 1 has demonstrated that the NaCl molecule is not dissociated by any number of water molecules. On the other hand, a pair of corner-site Na^+ and Cl^- is torn off by six water molecules. The two problems in the Introduction can thus be answered. Despite the smaller binding energy of $\text{Cl}^-\cdots\text{H}-\text{OH}$ compared to that of $\text{Na}^+\cdots\text{OH}_2$, the chloride ion exits first. The hydrogen bond enhanced by the "catalyst" sodium ions drives out the Cl^- ion. Despite drastic differences in the Na-Cl separation between Figures 1 and 2, binding energies at the B3LYP/6-311+G(2d,p) level are not very different, ~ 10 kcal/mol.¹⁵

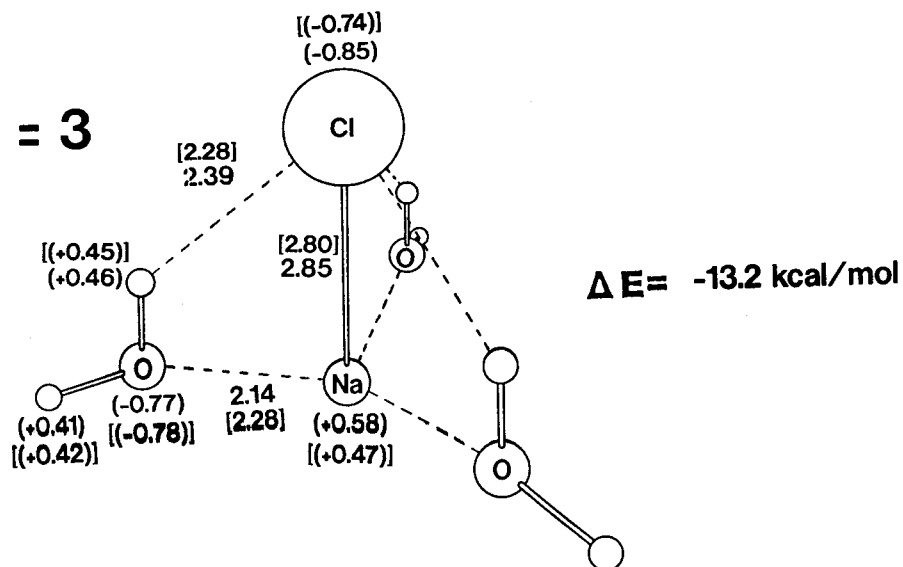
Figure 2 is reviewed. Dissociation models have been sought by trial and error. The analyses have not been systematic. We note that the $(\text{NaCl})_5$ part is not distorted so substantially in the $(\text{NaCl})_6(\text{H}_2\text{O})_n$ system. To search for the essential moiety of the $(\text{NaCl})_6$ cluster, we consider a $(\text{NaCl})_4(\text{H}_2\text{O})_n$ model next. The necessary number of water molecules for dissociation will be examined. In the model, the positions of three pairs of NaCl are fixed, and those of $\text{NaCl}\cdot(\text{H}_2\text{O})_n$ are optimized, i.e., $(\text{NaCl})_3\cdot\text{NaCl}\cdot(\text{H}_2\text{O})_n$. This small model is tractable computationally for the large number of n .

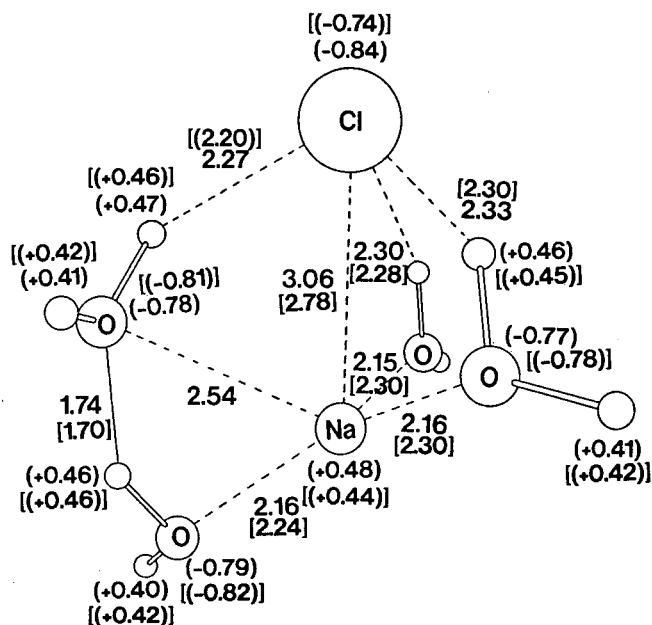
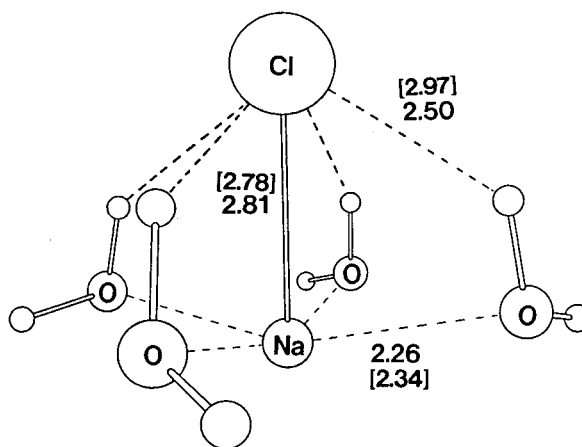
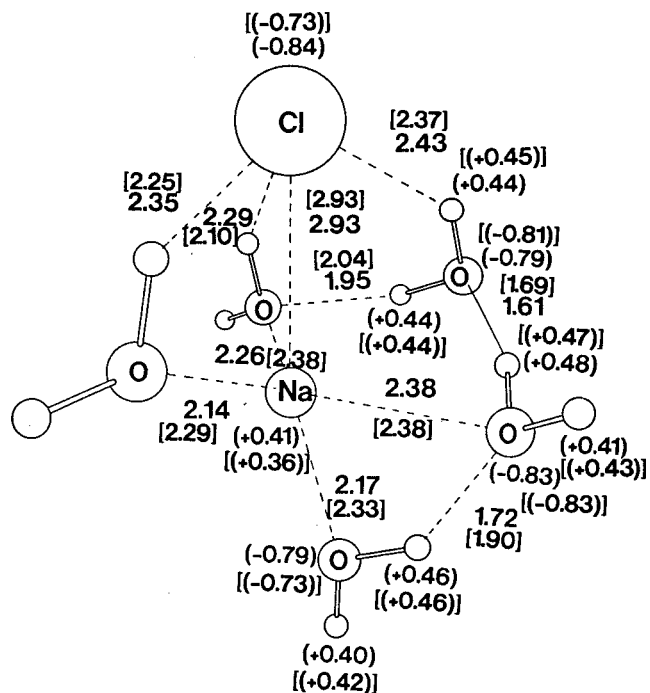
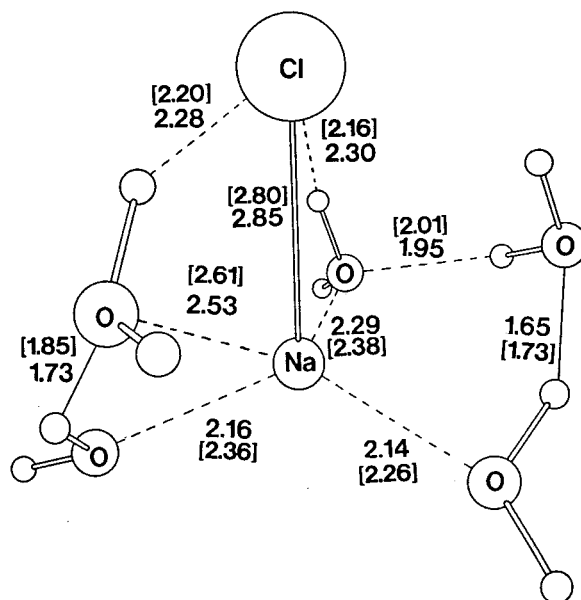
$$n = 0$$

$$n = 1a$$

$$n = 1b$$


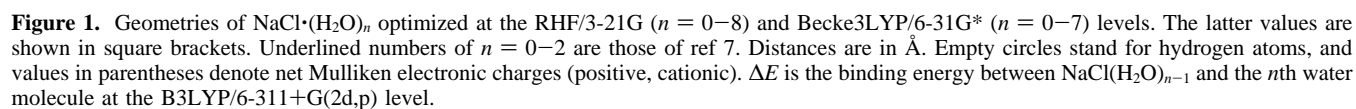
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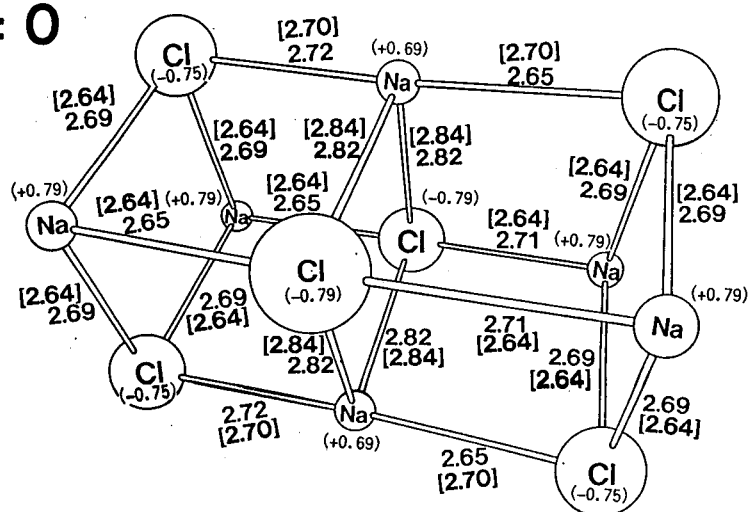
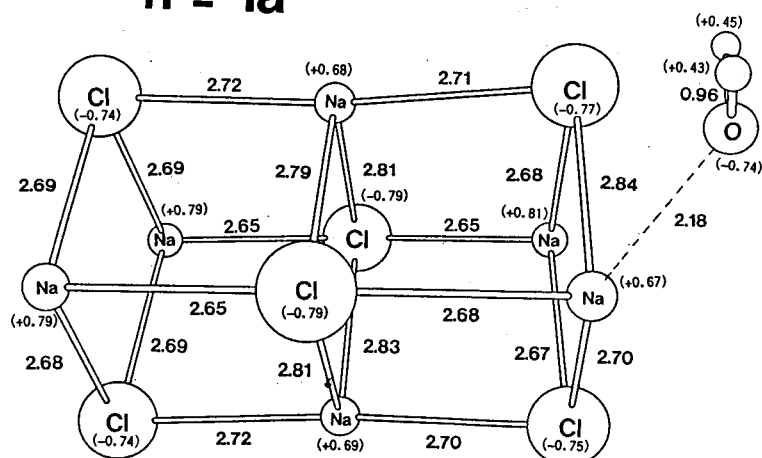
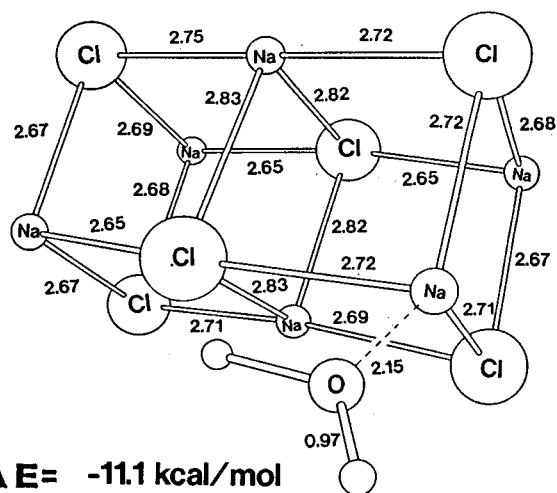
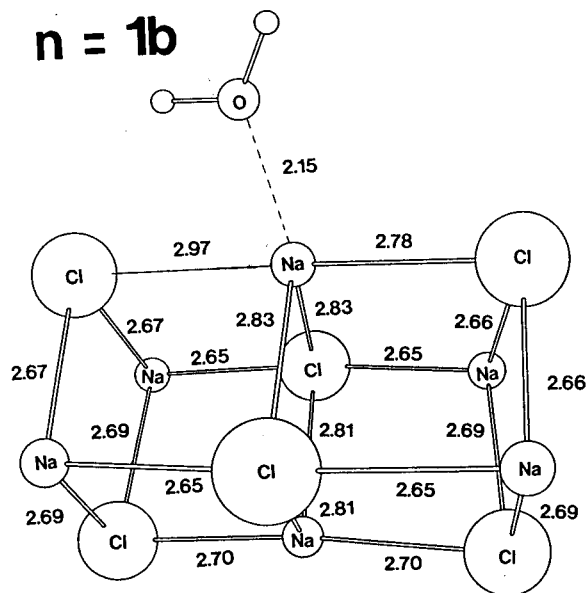
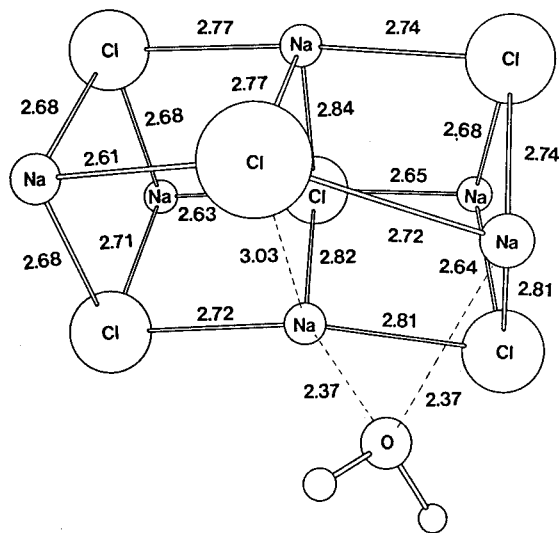


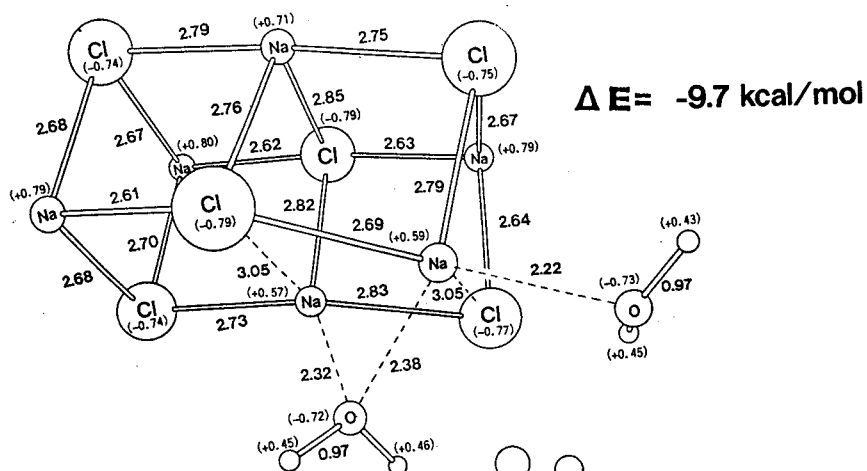
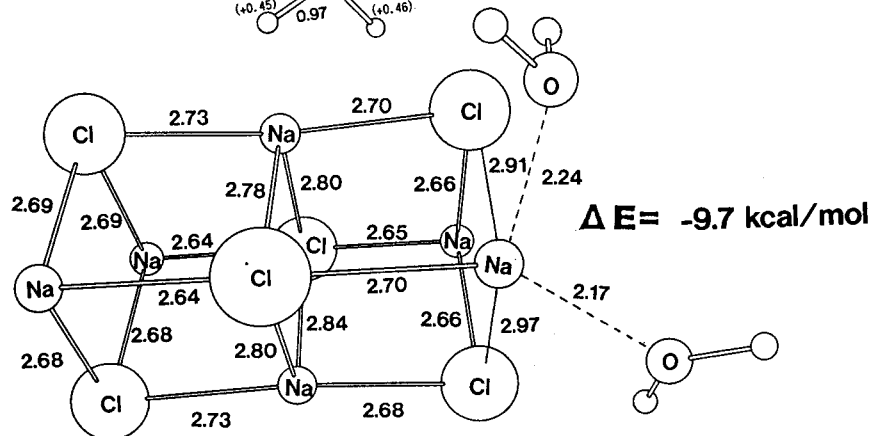
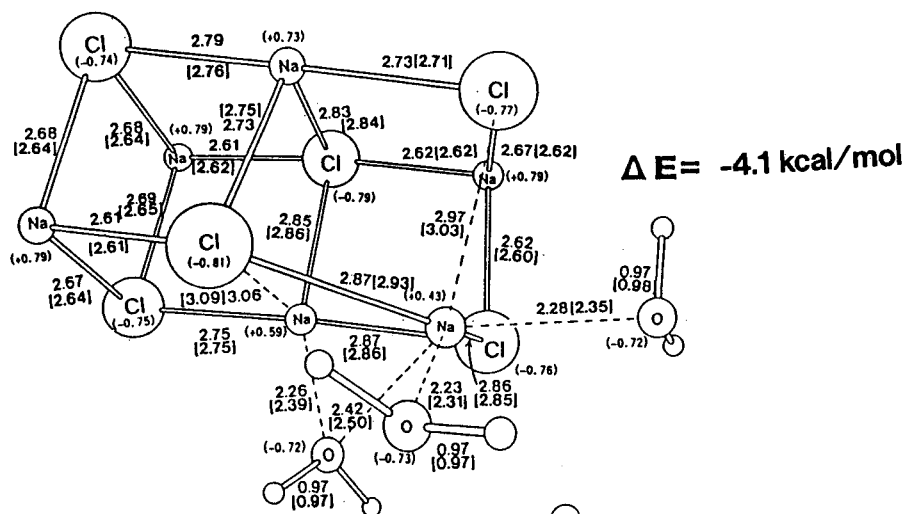
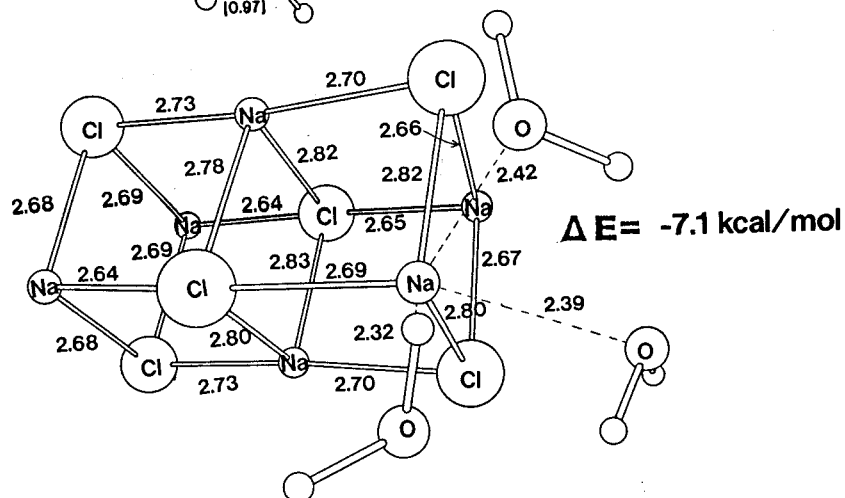
n = 3



n = 4a $\Delta E = -10.1$ kcal/mol**n = 4b** $\Delta E = -9.2$ kcal/mol**n = 5a** $\Delta E = -7.6$ kcal/mol**n = 5b** $\Delta E = -8.8$ kcal/mol



n = 0**n = 1a** $\Delta E = -11.8 \text{ kcal/mol}$ **n = 1c** $\Delta E = -11.1 \text{ kcal/mol}$ **n = 1b** $\Delta E = -10.1 \text{ kcal/mol}$ **n = 1d** $\Delta E = -4.9 \text{ kcal/mol}$

n = 2a**n = 2b****n = 3a****n = 3b**

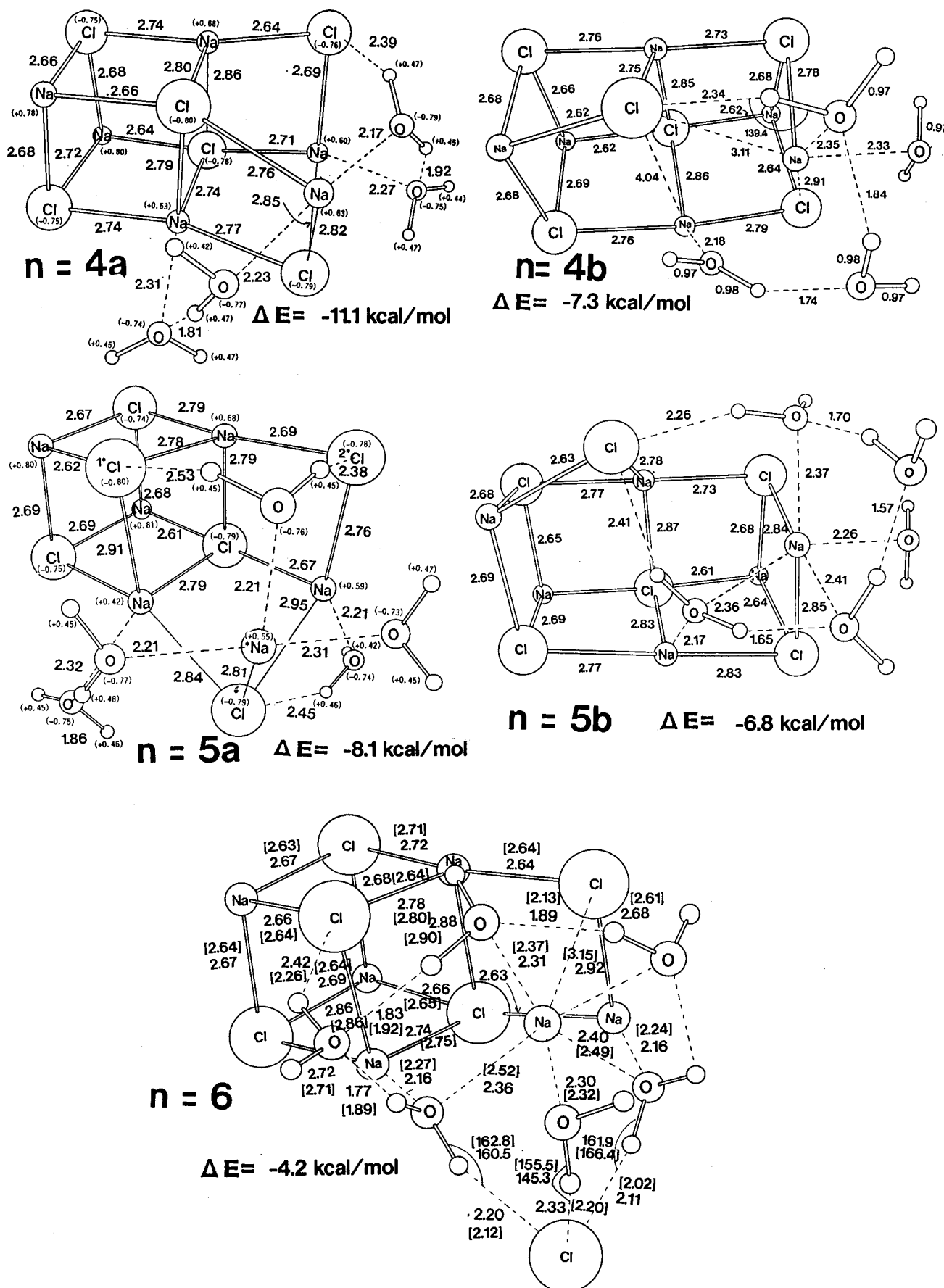


Figure 2. Geometries of $(\text{NaCl})_6(\text{H}_2\text{O})_n$ optimized fully at the RHF/3-21G ($n = 0-6$) and B3LYP/6-31(+)/G* ($n = 0, 3$, and 6) levels. When geometric isomers are shown, the stability order is $a > b > c \dots$, as calculated at the RHF/3-21G (not necessarily at the B3LYP/6-311+G(2d,p)) level.

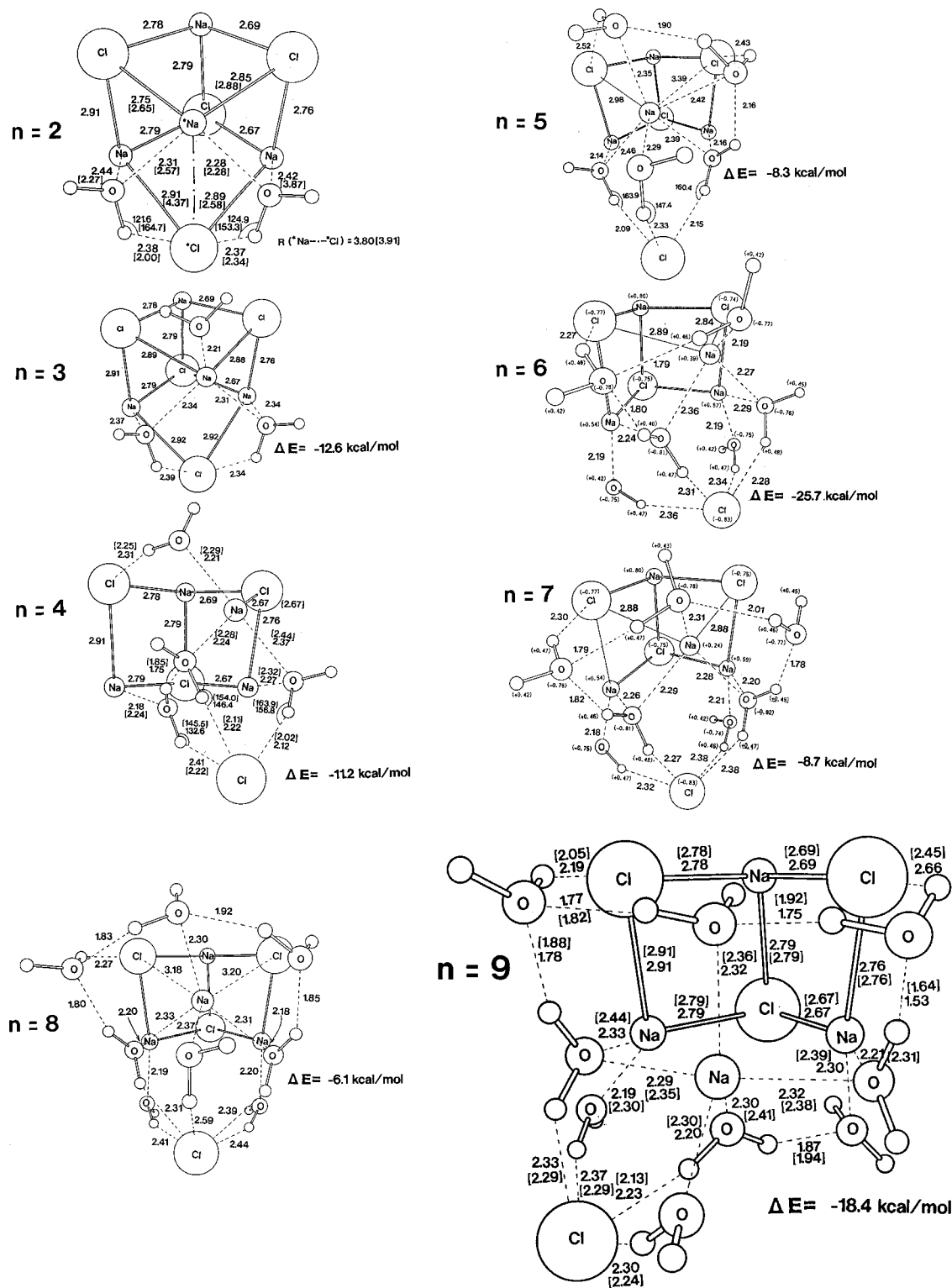
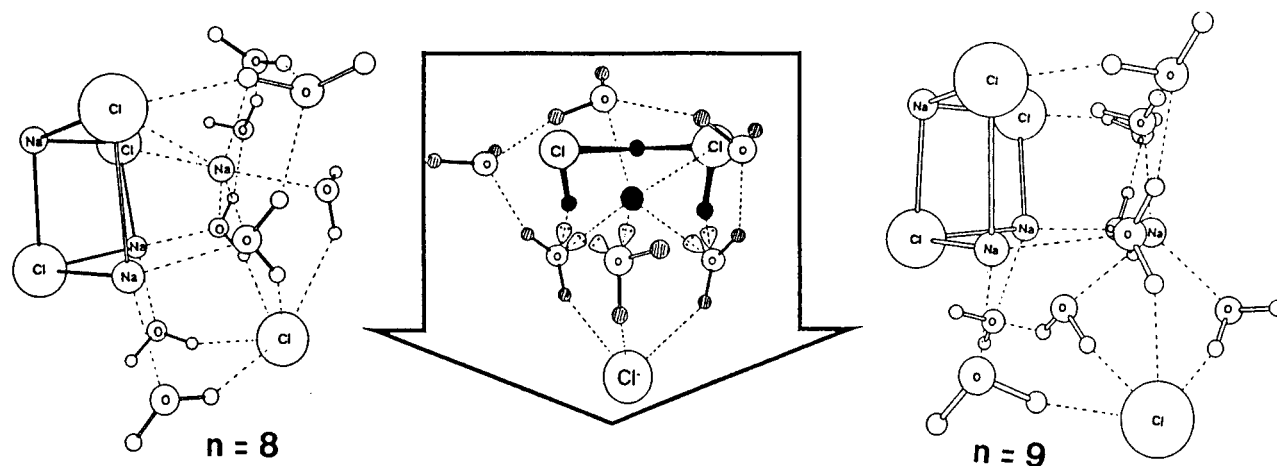
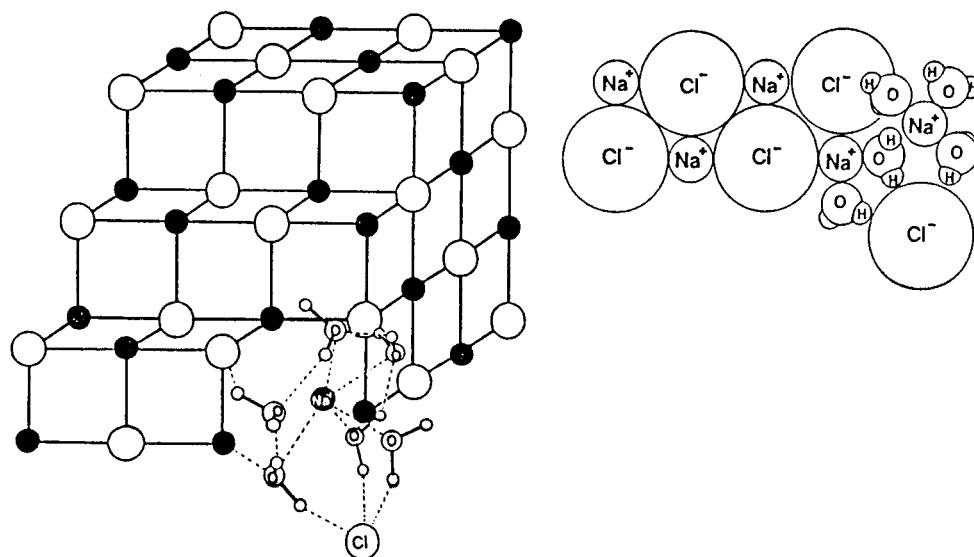


Figure 3. Geometries of $(\text{NaCl})_4 \cdot (\text{H}_2\text{O})_n$ optimized partially at the RHF/3-21G ($n = 0-9$) and B3LYP/6-31(+)G* ($n = 2, 4$, and 9) levels. The positions of three sodium and chloride ions are kept constant and are taken from those in $n = 5a$ of Figure 2. Those of the rest atoms, $\text{NaCl} \cdot (\text{H}_2\text{O})_1$, are fully optimized.

Figure 3 shows results of these partial optimizations. At $n = 2$, two H_2O molecules are arranged according to Scheme 2, and a Na-Cl bond is cleaved (3.80 Å, dashed line).¹⁶ At $n = 3$, a new H_2O molecule is placed onto the Na ion. As expected, the third H_2O molecule does not cause a significant geometric distortion. At $n = 4$, however, the third H_2O molecule on the upper side “pushes down” the Na^+ ion for the effective polarization of three intervening H_2O molecules. The Cl^- ion

is moved down substantially, while the Na^+ ion is still linked with a lattice chloride ion (2.67 Å). The $n = 4$ model is thus not sufficient to describe the dissociation. While the Cl^- ion can be separated readily by the hydrogen-bond directionality, the Na^+ ion is small and “hard”¹⁷ and retains the ionic bonds.

In the $n = 5$ model, the fifth H_2O molecule is coordinated to the Na^+ ion. However, the ion is still bound to a Cl^- lattice ion (2.98 Å). In the $n = 6$ model, the chloride ion is subject to four

SCHEME 3 : Mechanism of the Cooperative Dissociation of Two Ions through the H₂O AssociationSCHEME 4 Model of NaCl Crystals Broken by Water Molecules^a

^a Corner ions of $\text{Cl}^- \rightarrow \text{Na}^+ \rightarrow \text{Cl}^- \rightarrow \text{Na}^+$ are torn off successively.

hydrogen bonds and is completely separated from three neighboring Na^+ ions. Every H_2O molecule is involved in hydrogen and bridge bonds effectively to give a large stabilizing energy (25.7 kcal/mol). The $n = 7$ model is composed of four water molecules linked with the Cl^- ion and a water trimer. Although polarized water molecules are arranged effectively around the Na^+ ion, the ion is still bound to two lattice chloride ions. In the $n = 8$ model, the Na^+ ion is separated appreciably from those two lattice Cl^- ions (3.18 and 3.20 Å). In the $n = 9$ model, the Na^+ ion is eventually torn off and is surrounded by H_2O molecules (without ionic bonds). The $n = 9$ model describes a complete dissociation. Two ions are coordinated by water molecules and are distant from the $(\text{NaCl})_3$ cluster. The electrolytic dissolution of the NaCl crystal is thought to be the dissociation of a Na–Cl pair from a corner site of the crystal aided by nine water molecules. This suggestion is in line with that derived from a molecular dynamic simulation.^{2a}

IV. Concluding Remarks

The hydration and ion separation process of NaCl microclusters has been investigated by ab initio calculations. It is a question how and where water molecules pull out sodium and chloride ions from the crystal surface. First, a Na–Cl diatomic

molecule surrounded by water clusters was examined. However, the molecule does not undergo heterolytic dissociation with any number of water molecules. At most, the Na–Cl distance is elongated, 3.06 Å in the $n = 4$ model, relative to 2.42 Å in a free molecule. Next, cluster models $(\text{NaCl})_m(\text{H}_2\text{O})_n$ ($m = 6$ and 4) were examined. In most minimum-energy configurations, two lone-pair orbitals of a water molecule are directed toward two lattice sodium ions, which results in an enhanced acidity of the protons of the H_2O molecules and, consequently, in strong hydrogen bonds with a chloride ion. This directionality compels the ion to leave the corner lattice point. Water molecules polarized by the three sodium ions (two lattice and the leaving ions) drive out a chloride ion (see the criterion in Scheme 2). Scheme 3 exhibits a steric model for Scheme 2.

The large arrow indicates the direction of the ion departure.

In summary, nine water molecules are needed to cause the full dissociation of the NaCl unit from a salt aggregate: Coordination by two water molecules ($n = 2$) only elongates the Na–Cl bond. With $n = 4$, a chloride ion is pushed out while its partner sodium ion is still linked with a lattice chloride ion. At $n = 5$ –8, the Na–Cl bond is not broken completely.

This work has dealt with model clusters which are far from the NaCl dissolution in the aqueous media. However, from a microscopic point of view, Scheme 4 can be considered as

equivalent to Scheme 1 in the Introduction. Corner-site NaCl "molecules" are torn off successively.

References and Notes

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- (15) The RHF/3-21G binding energy for (NaCl)₆H₂O in $n = 1$ a of Figure 2 is computed to be 30.7 kcal/mol, which is unreasonably larger than the 11.8 kcal/mol calculated at the B3LYP/6-311+G(2d,p) level. The bases set superposition error (BSSE) is checked for the RHF/3-21G energy according to Boys and Bernardi counterpoise correction (Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553). The corrected RHF/3-21G energy is 17.5 kcal/mol, which is considerably smaller than 30.7 kcal/mol but still somewhat larger than the reliable value, 11.8 kcal/mol.
- (16) In general, RHF/3-21G geometries are found to be close to B3LYP/6-31(+)-G* ones. Exceptionally, there is a large difference in $n = 2$ (Figure 3). Since RHF/3-21G tends to overestimate the polarity of chemical bonds, a second Na-Cl ionic bond is retained, 2.91 Å, in $n = 2$. But the calculation at the B3LYP/6-31(+)-G* level gives a large distance, 4.37 Å. Fortunately, the Cl⁻ dissociation models do not involve such method dependence.
- (17) The ion radius of the Na⁺ ions is small (=0.97 Å), and the cation was classified to the hard-acid group (Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581).