Solvation of Sodium Chloride: An Effective Fragment Study of $NaCl(H_2O)_n$

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Calculations on NaCl microsolvated with up to 10 water molecules were performed by treating the NaCl with restricted Hartree−Fock (RHF) 6-31G(d) ab initio wave functions and the waters with the effective fragment potential (EFP) model. Increasing numbers of local minima are found with the addition of successive water molecules. As the number of waters is increased, the Boltzmann-averaged NaCl bond distance lengthens from 2.397 to 3.167 Å, the Mulliken charges increase to ±0.98, and the Boltzmann-averaged NaCl stretching frequency decreases from 359 to 94 cm^{-1}. The incremental binding energies (in kcal/mol) as a function of n are 15.4 ($n = 1$), 15.1 ($n = 2$), 14.0 ($n = 3$), 13.9 ($n = 4$), 12.3 ($n = 6$), 12.8 ($n = 8$), 9.1 ($n = 10$).

Introduction

The theoretical analysis of solvent effects on chemical phenomena has fostered considerable interest recently, since solvation plays an important role in the vast majority of chemical processes. One problem of fundamental importance is the manner in which the electronic and molecular structure of an electrolyte is modified by placing it in contact with a polar solvent. While it is clear that such a polar salt dissociates into solvated ions in bulk aqueous solution, it is not clear how the system progresses from a polar gas-phase molecule to dissociated ions as solvent molecules are added. The present work reports a systematic study of the effects of adding water molecules (up to 10 waters) on the molecular and electronic structure of NaCl, by representing NaCl with ab initio wave functions and the water molecules by the effective fragment potential (EFP) model.[1]

The solvation of a protic acid, such as HCl, may be monitored by detecting the formation of the hydronium ion H_3O^+, but no such simple species is available for a salt such as NaCl. Since the Na^+Cl^- ion pair will, theoretically, interact at any distance, there seems to be no direct definitive means to quantitatively determine the dissolved state of a salt. One approach to overcome this obstacle is to monitor the structure of the first solvation sphere around a salt molecule as a function of a generalized potential of mean force (PMF) which describes the average effect of a solvent on the energetics of the interaction between the pair of atoms or ions.[2] The inner minimum of the PMF is called a contact ion pair (CIP), while the outer minimum is referred to as a solvent-separated ion pair (SSIP). Whereas no solvent molecules lie between the atoms (Na^+, Cl^-) on average in the CIP, at least one solvent molecule *separates* the two in a SSIP. One may say that a CIP has one first solvation sphere, whereas a SSIP has (possibly overlapping) solvation spheres for each ion.

The progression from gas phase to CIP to SSIP is best modeled by a cluster approach, in which the NaCl and water molecules are treated explicitly. Ideally, the preferred approach is a fully ab initio one, in which the entire system is treated as a "supermolecule" using a high level of theory. Such an approach has been taken by Woon and Dunning in a study of several alkali halides in the presence of 1−3 water molecules.[3] Specifically, these authors (who also review the previous ab initio calculations on water-alkali halide clusters) investigated $NaCl{\cdot}(H_2O)_n$, with $n = 1$ and 2, using second-order perturbation theory (MP2[4]) with the correlation consistent aug-cc-pVDZ basis set.[5] For $n = 1$ Woon and Dunning find a low-energy cyclic C_1 minimum and a higher energy "cationic" C_{2v} local minimum connected by a C_s transition state. For $n = 2$ there is a C_2 structure, with the O of each water molecule bound to Na. The equilibrium NaCl bond distance is predicted to increase from 2.42 Å in the gas phase to 2.63 Å for $NaCl{\cdot}(H_2O)_2$. Concomitantly, the NaCl vibrational frequency decreases from 536 to 275 cm^{-1}.

Unfortunately, the rapidly increasing basis set size and the expected number of local minima on the potential energy surface preclude this approach beyond a small number of waters. An alternative that is used in the current work is to treat the solute NaCl with an ab initio wave function and the water molecules by the effective fragment potential (EFP) model[6−8] that has proved to be quite successful in several recent applications. This method closely matches the ab initio energetics for the internal rotation in formamide in the presence of up to four waters,[6] for the low-energy UV excitations in formamide as waters are added,[7] and for the effect of increasing numbers of water molecules in the Menshutkin reaction.[8] The method also closely reproduces the ab initio relative isomer energies and barrier heights for small water clusters.[9]

There have been some simulations of NaCl in the presence of water molecules using model potentials. Smith and Dang,[2] using a polarizable potential, determined the PMF for NaCl in the presence of 216 water molecules and found a CIP minimum at a Na−Cl separation of ~3 Å and a SSIP minimum at ~5 Å, separated by a barrier of about 1.8 kcal/mol. Asada and Nishimoto[10] predicted a gradual solvation of NaCl by considering $NaCl(H_2O)_n$ clusters for $n = 0-8$ modeled with a Monte Carlo simulation, using a Honda−Kitaura bond−bond potential.[11]

Theoretical/Computational Methods

A. Effective Fragment Potential Method. The EFP method has been described in detail elsewhere, so only its salient features will be briefly summarized here. The model treats each solvent

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molecule explicitly, by adding one-electron terms directly to the ab initio Hamiltonian,

$$H = H_{\mathrm{AR}} + V \quad (1)$$

where H_{AR} is the ab initio Hamiltonian that describes the "action region" (AR) of the system. There are three one-electron terms in V, representing the potential due to the solvent (fragment) molecules. For the ith solvent molecule at nuclear position R, the effective fragment potential of interaction with the solute is given by

$$V_{\mathrm{el}}^{(\mathrm{efp})}(i,R) = \sum_{k=1}^{K} V_k^{\mathrm{Elec}}(i,R) + \sum_{l=1}^{L} V_l^{\mathrm{Pol}}(i,R) + \sum_{m=1}^{M} V_m^{\mathrm{Rep}}(i,R) \quad (2)$$

The three terms on the right-hand side (RHS) of eq 2 represent the electrostatic (Coulombic), polarization, and exchange repulsion/charge transfer interactions, respectively. Similar terms are added to represent the interactions between solvent molecules. The solute (including the desired number of solvent molecules) is explicitly treated with the ab initio wave function of choice, while the remainder may be represented by effective fragments.

An accurate, relatively compact, representation of the electrostatic potential in the important interaction regions is achieved using a *distributed* multipolar analysis[12] (DMA) of the fragment charge distributions. K in the first term of eq 2 is the number of expansion points. In the present implementation, each nuclear center and each bond midpoint is chosen to be an expansion point (e.g., five expansion points for a water molecule), and the expansion is extended through octupoles. Since such a multipolar expansion is a point charge model, it must be modified to account for overlapping electron densities as the molecules (fragment and solute or fragment and fragment) approach each other. This is accomplished by multiplying the expansion by a distance-dependent cutoff function.[1] The polarization of the fragment molecules by the electric field of the solute (ab initio) molecules (second term in eq 2) is treated by a self-consistent perturbation model employing bond and lone pair localized orbital dipole polarizabilities extracted from finite-field perturbed Hartree−Fock calculations on isolated spectator (fragment) molecules and centered at the centroids of the L localized orbitals ($L = 4$ for water).

The exchange-repulsion/charge-transfer interaction between the solute and solvent molecules is modeled by one-electron terms in the ab initio Hamiltonian that have the form of simple Gaussian functions located at the solvent atom centers. The Gaussian functions are optimized by a fitting procedure, based on a set of 192 ab initio water dimer geometries. The ab initio exchange repulsion/charge-transfer potential $E_{\mathrm{rem}}^{(\mathrm{ab})}$ is obtained by subtracting the sum of the electrostatic plus polarization energies from the total ab initio potential. Then, V_m^{Rep} in eq 2 is fitted to $E_{\mathrm{rem}}^{(\mathrm{ab})}$. The fragment−fragment interactions are treated in the same way, using an exponential form for V_m^{Rep}, and are easily added to the Hamiltonian.

The internal fragment geometries are fixed, but their relative orientations are allowed to relax. The necessary equations have been derived[1] and coded for the analytic gradients of the entire (ab initio + fragments) system. The availability of analytic gradients means that one can also perform vibrational analyses using finite differences of these gradients. So, one can determine the manner in which geometries and energetics of minima, transition states, and reaction paths (and therefore the reaction dynamics) are modified by the presence of the solvent. The entire code described here is available in the electronic structure code GAMESS.[13]

B. Computational Methods. The NaCl was treated at the restricted Hartree−Fock (RHF) level of theory with the 6-31G(d) basis set,[14] while the water molecules were represented by the effective fragment potential (EFP) method described above. For each $\mathrm{NaCl(H_2O)}_n$ cluster, full geometry optimizations (within the constraint of frozen internal water geometries) were performed from several starting structures. The number of starting structures generally increased in number with increasing n. At each optimized geometry a numerical Hessian (matrix of energy second derivatives) was obtained from finite double differences of analytic gradients, to determine if these stationary points are minima (positive definite Hessian) or mth order saddle points (m negative eigenvalues). For each unique minimum the structural and vibrational information was used to determine zero point corrections to the energy, as well as enthalpy and entropy contributions at 298 K, using simple rigid rotor−harmonic oscillator partition functions. Mulliken populations were monitored to provide a qualitative trend in the atomic charges as a function of n. For the smaller clusters, single point fully ab initio calculations were performed at the EFP geometries, using second-order perturbation theory (MP2[4]) and the 6-311++G(d,p) basis set.[15]

Results and Discussion

A. Zero, One, and Two Water Molecules. The only previous ab initio study of NaCl−water clusters was the MP2/aug-cc-PVDZ investigation of up to two water molecules by Woon and Dunning.[3] It is useful to compare these results with those obtained from the combined Hartree−Fock (HF)/EFP calculations from the present work. Properties that may be compared are molecular structures, intermolecular vibrational frequencies (recall that the *internal* fragment water geometries are fixed) and the incremental binding energies. The latter are defined by Woon and Dunning as

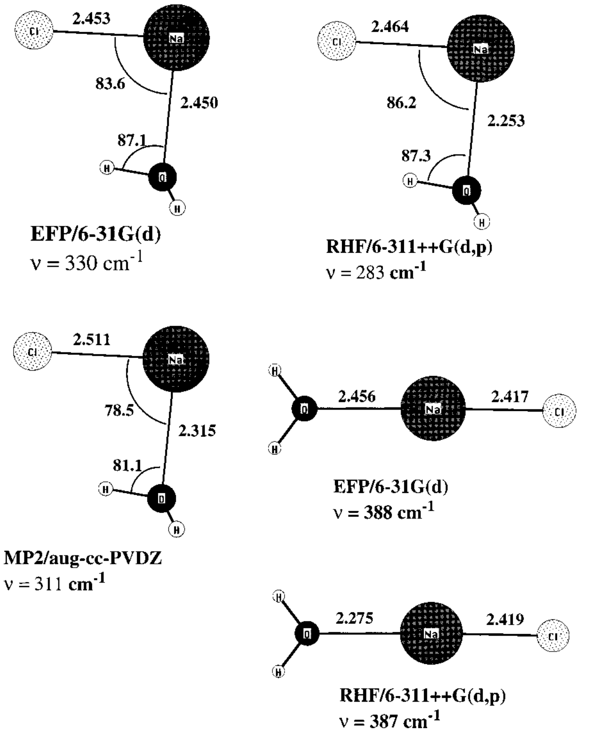
$$\Delta E_{n-1,n} = \Delta E_n - \Delta E_{n-1} \quad (3)$$

for the reaction

$$\mathrm{NaCl(H_2O)}_{n-1} + \mathrm{H_2O} \rightarrow \mathrm{NaCl(H_2O)}_n$$

Woon and Dunning find $\Delta E_{n-1,n} = -17.5$ and -16.8 kcal/mol for $n = 1$ and 2, respectively. The corresponding HF/EFP results are -15.4 and -15.1 kcal/mol. This is quite reasonable agreement, especially since the current implementation of the EFP method[1] is based on Hartree−Fock theory, and one expects some modification of energetics when perturbation corrections are added.

Molecular structures and vibrational frequencies are best considered relative to those for the gas-phase molecule. The RHF/6-31G(d) NaCl bond length and vibrational frequency are 2.397 Å and 359 $\mathrm{cm^{-1}}$, respectively. These may be compared with the MP2/aug-cc-pVDZ values of 2.408 Å and 345 $\mathrm{cm^{-1}}$. The structures and related vibrational frequencies for two low-lying $\mathrm{NaCl(H_2O)}$ complexes are shown in Figure 1. The structure that is predicted to be lowest in energy by Woon and Dunning has a roughly 90° Cl−Na−O angle. The Na−Cl distances predicted by the three levels of theory (MP2/aug-ccPVDZ, EFP/6-31G(d), and RHF/6-311++G(d,p)) are in good agreement with each other and reflect an increase relative to the isolated gas-phase compound. The concomitant decrease in the Na−Cl vibrational frequency predicted by the three levels of theory is also in good agreement, about 30 $\mathrm{cm^{-1}}$. Of course,



EFP/6-31G(d) ν = 330 cm^{-1}

RHF/6-311++G(d,p) ν = 283 cm^{-1}

MP2/aug-cc-PVDZ ν = 311 cm^{-1}

EFP/6-31G(d) ν = 388 cm^{-1}

RHF/6-311++G(d,p) ν = 387 cm^{-1}

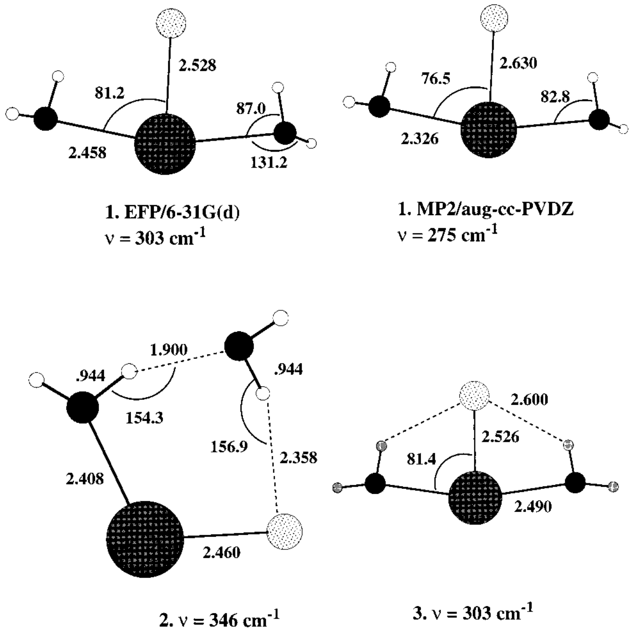
Figure 1. Structures and frequencies for NaCl·H_2O.

the molecular vibrations, especially those of comparable frequency, are often coupled, so except for the parent diatomic, the quoted NaCl frequencies are those that correspond most closely to the Na−Cl stretch. The one geometrical feature that is not well reproduced by the EFP method is the Na−O internuclear distance. The greater than 0.1 Å overestimation of this distance is likely a reflection of the fact that the EFP model is developed for weak, hydrogen bond-like interactions, while the Na−O interaction is likely to be stronger.

Woon and Dunning also reported a second NaCl(H_2O) C_{2v} isomer, although the geometry for this isomer is not given. The EFP and RHF/6-311++G(d,p) geometries for this second isomer are given in Figure 1. As for the first isomer, the Na−Cl distances are in good agreement, while the EFP method overestimates the Na−O distance. Woon and Dunning note that this structure has two very small vibrational frequencies of 20−60 cm^{-1}. The EFP method predicts these two frequencies to be 13 and 16 cm^{-1}. The MP2/aug-cc-pVDZ energy for the second isomer is 4.6 kcal/mol relative to the first, global minimum. This may be compared with the EFP value of 0.7 kcal/mol and the MP2 (RHF)/6-311++G(d,p) value of 3.3 (1.0) kcal/mol. So, the EFP and RHF results are quite close, despite the basis set difference.

A third NaCl(H_2O) structure that is similar to the global minimum, but is totally planar, is predicted to lie 0.6 kcal/mol higher in energy than the global minimum shown in Figure 1. This structure was not reported by Woon and Dunning. All of the isomers will be discussed further in the next section.

Woon and Dunning report only one NaCl$(H_2O)_2$ isomer, whose main geometric features are compared with the EFP results in Figure 2. The two levels of theory are mostly in good agreement with each other, except for the Na−O distance, which is again predicted by the fragment method to be too long. Both methods predict a significant increase in the Na−Cl bond length with the addition of the second water (0.075 Å for EFP, 0.119 Å for MP2) and a concomitant increase of about 30 cm^{-1} in the Na−Cl stretching frequency.



1. EFP/6-31G(d) ν = 303 cm^{-1}

1. MP2/aug-cc-PVDZ ν = 275 cm^{-1}

2. ν = 346 cm^{-1}

3. ν = 303 cm^{-1}

Figure 2. Structures and frequencies for NaCl·$(H_2O)_2$

Two additional NaCl$(H_2O)_2$ isomers, labeled **2** and **3** in Figure 2, are found at the EFP/6-31G(d) level of theory. In isomer **2** the two water molecules are hydrogen bonded to each other. One of these is bound to Na through its oxygen, while the second water is hydrogen bonded to the Cl through one of its hydrogens. Isomer **3** is a completely planar analogue of the global minimum **1**, with slightly elongated Na−O distances. The energies of **2** and **3** relative to **1** are 0.01 and 1.3 kcal/mol, respectively. For comparison, single point RHF/6-31G(d) and MP2/6-311++G(d,p) calculations were performed at the EFP/6-31G(d) geometries for these three isomers. The RHF and MP2 relative energies for isomers **1, 2, 3** are (0.0, 1.1, 1.9) and (0.0, 0.1, 0.1) kcal/mol, respectively.

One can conclude from the foregoing comparisons between the EFP and fully ab initio results that the EFP method produces quite reasonable agreement with the more accurate level of theory for both structures and energetics. In the following section, the results of EFP calculations on larger NaCl$(H_2O)_n$ clusters are discussed.

B. NaCl$(H_2O)_n$, $n = 4, 6, 8, 10$. The two lowest energy minima on the potential energy surfaces for clusters of 4, 6, 8, and 10 waters with NaCl are shown in Figure 3. The key structural and energetic features for these structures are contained in the figure and in Tables 1 and 2. Full structural details, as well as animations of all normal vibrational modes generated using MacMolPlt.[16] may be viewed on the web.[17]

Several general trends are apparent in the tables. As the number of waters is increased, the Na−Cl internuclear distance increases, the frequency most closely associated with the Na−Cl stretch decreases, and the charge separation between Na and Cl increases toward ±1. Also listed in Tables 1 and 2 are the relative enthalpies and free energies of the isomers, at 0 and 298 K, respectively. The majority of the isomers for a given number of waters lie within a 5 kcal/mol range, so many of these structures will be accessible at room temperature. It is unlikely that all structural isomers have been found, but the predicted trend of increasing separation of the Na^+ and Cl^- ions as the number of waters increases will not be qualitatively altered. To make this trend more apparent, the Boltzmann-averaged vibrational frequencies and NaCl distances, based on the calculated ΔG_{298} values, have been calculated for each value

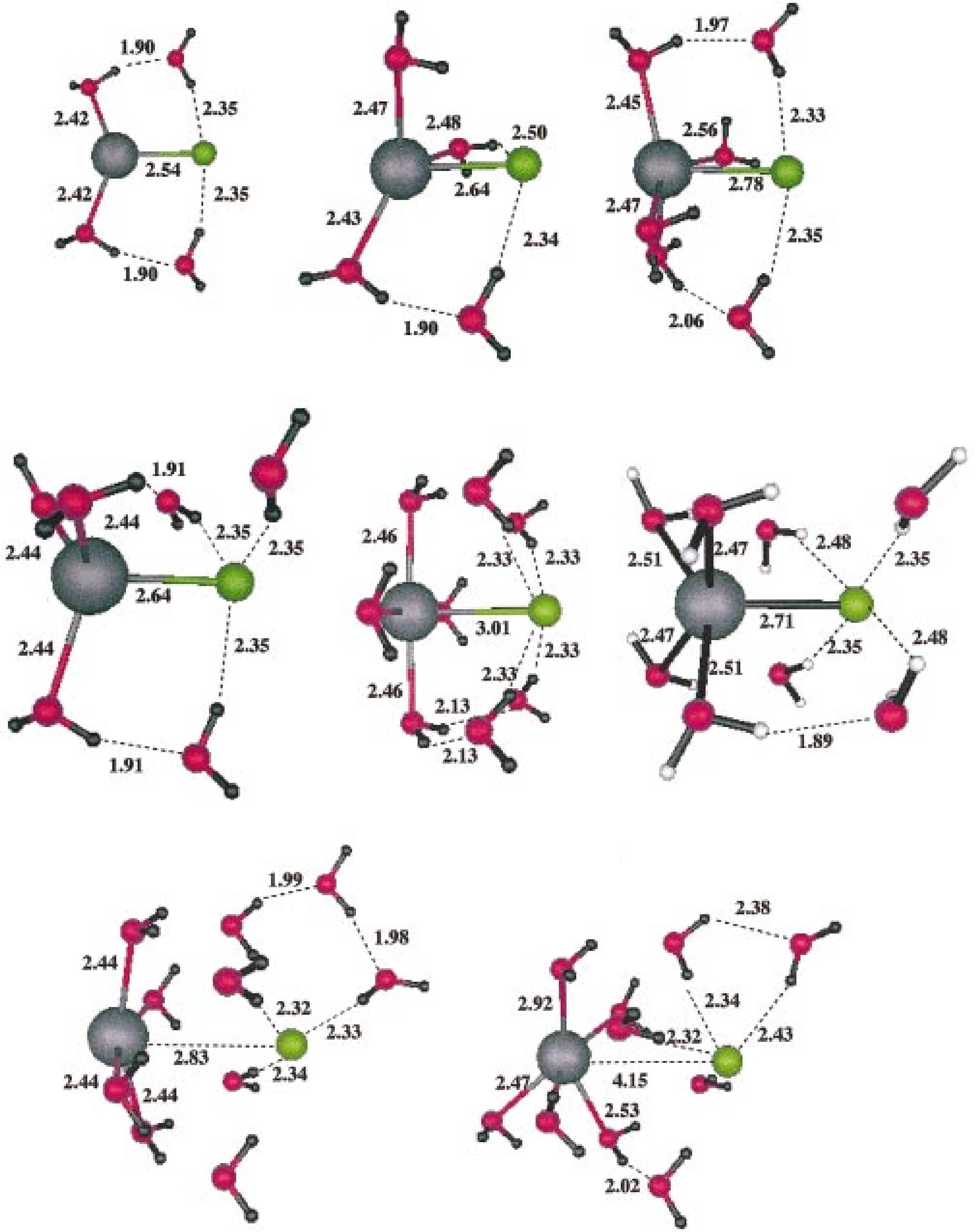


Figure 3. Structures for lowest two isomers for NaCl$\cdot$(H_2O)$_n$, $n = 4, 6, 8, 10$.

of n and are listed in Tables 1 and 2. The corresponding frequencies (distances) for $n = 0, 1, 2$ are 359 (2.4), 387 (2.420), and 309 (2.590) cm^{-1} (Å), respectively. As expected, except for $n = 1$, there is a general decrease in the frequencies as the number of waters is increased. Similarly, there is a monotonic increase in the NaCl distance.

The incremental binding energies, as defined in eq 3 are summarized in Table 3. These are obtained from the electronic

TABLE 1: Structural and Energetic Quantities for $NaCl(H_2O)_4$ and $NaCl(H_2O)_6$[a]

structure	R(NaCl)	ν	q	ΔH_0	ΔG_{298}	$\langle \nu \rangle^b$	$\langle R \rangle^b$
			Four Waters				
1	2.54	286	0.82	0.0	0.0		
2	2.64	233	0.87	0.5	0.7		
3	2.64	234	0.87	0.6	0.4		
4	2.68	231	0.88	1.2	1.5		
5	2.55	326	0.82	1.9	3.1		
6	2.75	250	0.91	1.8	2.7		
7	2.53	257	0.81	3.0	2.5		
8	2.56	252	0.83	3.7	3.5		
9	2.46	393	0.75	7.9	6.6	261	2.590
			Six Waters				
1	2.64	257	0.88	0.0	0.0		
2	2.78	221	0.91	0.8	3.0		
3	2.65	219	0.87	2.5	4.7		
4	2.86	229	0.93	2.3	4.6		
5	2.66	267	0.88	2.0	3.0		
6	2.76	211	0.91	2.5	4.2		
7	2.56	325	0.83	4.0	6.2		
8	2.63	207	0.87	2.5	2.1		
9	2.64	222	0.87	2.8	2.4		
10	2.66	202	0.89	3.3	3.4		
11	2.53	210	0.82	4.4	3.5		
12	2.56	208	0.84	5.0	4.4		
13	2.58	208	0.85	5.7	5.5		
14	2.53	249	0.82	5.9	4.5		
15	2.64	229	0.87	6.4	6.8		
16	2.63	203	0.87	6.5	5.1		
17	2.51	221	0.80	8.9	9.0		
18	2.53	246	0.82	11.7	8.2	254	2.641

[a] R is in Å, ν is in cm^{-1}, q is the charge on Na, and ΔH_0 and ΔG_{298}, in kcal/mol, are energies relative to the lowest energy isomer. [b] Boltzmann-averaged values, using relative ΔG_{298} values: frequencies in cm^{-1}, distances in Å.

TABLE 2: Structural and Energetic Quantities for $NaCl(H_2O)_8$ and $NaCl(H_2O)_{10}$[a]

structure	R(NaCl)	ν	q	ΔH_0	ΔG_{298}	$\langle \nu \rangle^b$	$\langle R \rangle^b$
			Eight Waters				
1	3.01	166	0.95	0.0	0.0		
2	2.71	187	0.90	2.1	0.2		
3	2.59	215	0.85	5.6	4.8		
4	2.74	198	0.92	4.4	0.3		
5	2.67	149	0.89	5.0	1.2		
6	2.72	131	0.91	5.2	2.1		
7	2.64	155	0.89	6.1	2.0		
8	2.70	210	0.91	6.5	2.7	178	2.834
			Ten Waters				
1	3.83	27	0.98	0.0	0.0		
2	4.15	43	0.98	−0.1	0.7		
3	2.73	130	0.91	0.2	−0.3		
4	4.15	43	0.99	1.6	2.9		
5	4.21	45	0.99	1.7	1.9		
6	2.71	129	0.92	2.5	1.8		
7	2.74	148	0.92	2.8	1.6		
8	3.07	165	0.96	2.4	1.3		
9	2.87	104	0.94	1.6	0.4		
10	2.84	117	0.94	2.7	1.7		
11	2.66	255	0.89	4.1	2.7		
12	2.77	152	0.93	3.2	1.5		
13	4.06	15	0.98	6.9	5.3		
14	2.79	122	0.93	5.8	4.1	94	3.167

[a] R is in Å, ν is in cm^{-1}, q is the charge on Na, and ΔH_0 and ΔG_{298}, in kcal/mol, are energies relative to the lowest energy isomer. [b] Boltzmann-averaged value, using relative ΔG_{298} values: frequencies in cm^{-1}, distances in Å.

TABLE 3: Incremental Binding Energies for $NaCl(H_2O)_n$, kcal/mol

n	$\Delta E_{n-1,n}$	n	$\Delta E_{n-1,n}$
1	15.4	**6**	12.3
2	15.1	**8**	12.8
4	13.9	**10**	9.1

energies of the lowest energy isomer for each value of n, uncorrected for vibrational zero point energies. There is a steady, but not monotonic, decrease in $\Delta E_{n-1,n}$ with increasing n. One would expect this trend to continue as NaCl becomes fully solvated.

Summary and Conclusions

The effective fragment potential (EFP) model has been used to study the effect of adding increasing numbers of waters on several properties of NaCl. The addition of a relatively small number of waters results in a nearly complete separation of charge and substantial stretching of the NaCl bond. The latter is accompanied by a concomitant reduction of the Na−Cl stretching frequency to about 100 cm^{-1}, from the gas-phase value of ~350 cm^{-1}.

Analysis of the structures in Figure 3 and the incremental binding energies in Table 3 clearly suggest that NaCl in the presence of 10 water molecules is far from fully solvated. $NaCl(H_2O)_{10}$ is a contact ion pair, not a separated ion pair, and it is likely that many more water molecules are needed to attain the latter state. A simple calculation reveals that NaCl + 10 water molecules comprises a very concentrated (~6 M) solution. A dilute solution would require 2−3 orders of magnitude more waters. Such calculations are certainly feasible with the efficient and accurate EFP method, and simulations using molecular dynamics or Monte Carlo methods will be presented in future work. Even for a modest number of solvent molecules, Monte Carlo or molecular dynamics simulations are more efficient and reliable methods for detecting local minima and determining average properties.

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