# The Pronounced Effect of Microsolvation on Diatomic Alkali Halides: *Ab Initio* Modeling of $MX(H_2O)_n$ ($M = Li, Na$; $X = F, Cl$; $n = 1-3$)

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**Abstract:** *Ab initio* cluster calculations are reported in which the diatomic alkali halide (MX) species LiF, LiCl, NaF, and NaCl are microsolvated with up to three water molecules. Second-order Møller–Plesset perturbation theory (MP2) was used in conjunction with correlation consistent basis sets: cc-pVDZ (Li, Na) and aug-cc-pVDZ (F, Cl, O, H). Cyclic structures, with $C_1$, $C_2$, and $C_3$ symmetries respectively, were found for the addition of one, two, and three water molecules. Harmonic frequencies were determined for the one and two water clusters in order to verify that these are true minima. For the one water cluster, a local minima of $C_{2v}$ symmetry was also characterized, as well as the transition state between the two equivalent cyclic structures. The incremental binding energies for the successive addition of water molecules tend to be comparable within each species and very similar between different species as well. The incremental binding energies (in kcal/mol) for each species were: $LiF(H_2O)$ [−20.3], $LiF(H_2O)_2$ [−19.2], $LiF(H_2O)_3$ [−16.8]; $LiCl(H_2O)$ [−20.2], $LiCl(H_2O)_2$ [−19.0], $LiCl(H_2O)_3$ [−16.9]; $NaF(H_2O)$ [−21.9], $NaF(H_2O)_2$ [−23.1]; and $NaCl(H_2O)$ [−17.5], $NaCl(H_2O)_2$ [−16.8]. The metal–halogen bond was found to lengthen appreciably with increasing degree of solvation. In the $LiCl(H_2O)_n$ series, the gas-phase LiCl equilibrium bond length of 2.088 Å (MP2) increased to 2.440 Å upon addition of three water molecules, an increase of 0.352 Å. Zero-point energy contributions, cluster frequency shifts, partial charges, and the effect of basis set superposition error were also investigated. Other topics include the trends in the solvation dependence of the ionic asymptotes as well as an alternative acid–base channel for $MX(H_2O)$.

## Introduction

Solvation effects can profoundly alter chemical and physical interactions. Diatomic alkali halides (MX) are bound by 100 to 140 kcal/mol with respect to dissociation into neutral atoms in the gas phase,[1] but a crystalline sample of the corresponding salt dissociates readily into ions when placed in aqueous solution. Understanding the microscopic behavior of salts in solution is one of the most fundamental issues in chemistry. Solvation effects in four alkali halides have been investigated in this work by considering clusters of LiF, LiCl, NaF, or NaCl with up to three water molecules. While this microsolvation model cannot be expected to quantitatively predict the effects of liquid-phase solvation on these salts, it can be expected to provide valuable insights into the forces controlling the arrangement of the solvent around the $M^+$ and $X^-$ ions and the effect of solvation on the MX bond. In addition, the results of these studies provide stringent tests of the potentials developed to model aqueous solutions of alkali halide salts.

Regardless of the environment, the ground states of the diatomic alkali halides are strongly ionic near the vicinity of the equilibrium structure, but different products are more stable in and out of water. In the gas phase, neutral products are favored as the nuclei are separated; they are reached by means of an avoided crossing with the potential curve arising from the neutral atoms. In aqueous solution, on the other hand, the ions are favored as dissociation products because of the strong stabilizing interactions between the charged species and the polar solvent. Researchers who perform solution simulations (see, for example, ref 2) usually discuss the $M^+-X^-$ interactions in solution in terms of a potential of mean force (PMF), which describes the average effect of the solvent upon the energetics of the pair interaction. The PMF for an ion pair in solution often exhibits two or more minima. The inner minimum is known as a contact ion pair (CIP). It possesses a structure in which no water molecules are interposed between the ions. The depth of the PMF for the CIP represents the binding energy of the MX molecule in solution and is just a few kilocalories per mole for the alkali halides. The outer minimum is known as a solvent-separated ion pair (SSIP). The barrier separating the first two minima represents the energy necessary to insert water between the two ions and disrupt the direct bonding interaction.

The cluster method is a promising approach for studying the onset of solution behavior and has been elegantly referred to as the microsolvation model. Although we are currently unable to treat clusters much beyond $MX(H_2O)_3$ at the present level of theory with state-of-the-art quantum chemical technology, these results provide a valuable starting point for assessment of lower levels of quantum theory and of the efficacy of semiempirical potentials for use in simulations of larger clusters or solutions. At the same time, the change in behavior resulting from the addition of even the first three waters already exhibits intriguing trends. As we will show, the MX bond lengthens dramatically and the binding relative to the $M^+ + X^-$ ions decreases substantially as water molecules are added to the cluster (although the relative stabilization of MX vs $M^+ + X^-$ remains very much in favor of the neutral atoms).

To date, few *ab initio* calculations have been performed on MX–water clusters, and only one published effort has proceeded

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(2) Smith, D. E.; Dang, L. X. *J. Chem. Phys.* **1994,** *100,* 3757.

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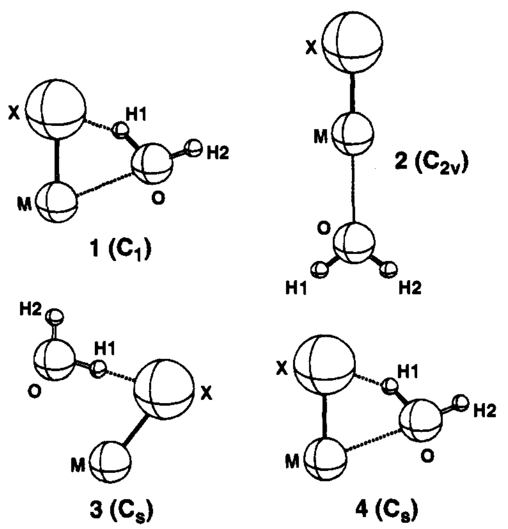

**Figure 1.** Structures of $MX(H_2O)$ configurations investigated in this work. Structure **1** is the $C_1$ cyclic global minimum; M, X, O, and H1 are nearly coplanar, and H2 is out-of-plane (see Figure 2 for identification of parameters). Planar structures **2** and **3** favor the cationic $M^+-O$ and anionic $X^--H1$ interactions, respectively. Structure **4**, also planar, is the transition state between left- and right-handed conformers of **1**. Note that structures **1**, **2**, and **4** are critical points on the surface, but no minimum or transition state was found that resembles structure **3**.

beyond the Hartree−Fock (HF) level. The investigation of Kulkarni and Rao[3] is the only work which has examined all four of the $MX(H_2O)$ clusters considered here and is the only work that addresses $NaF(H_2O)$ and $NaCl(H_2O)$. Their low-level calculations (HF/STO-3G) predict bond energies generally much larger than those found in the current work, perhaps due to excessive BSSE and/or overestimation of electrostatic properties. For all four species, they report an optimum geometry that possesses $C_s$ symmetry, with the water bent out of plane from a planar $C_{2v}$ structure (see 2 in Figure 1) that lies slightly higher in energy. Szczęśniak *et al.*[4] have also studied $LiCl(H_2O)$ at the HF level using slightly better 4-31G basis sets. They found the $C_{2v}$ structure to be lowest in energy. Kaufmann *et al.*[5] are the only previous workers to consider the effects of correlation on the alkali halide−water clusters. They also found the $C_{2v}$ structure to be the most stable structure for $LiF(H_2O)$. Their binding energy of −20.9 kcal/mol (MP2/6-31+G*) is similar to our value for that geometry. Singh and Knözinger[6] reported a cyclic minimum (see **1** in Figure 1) for LiF and LiCl with one water at the HF/6-31+G level of theory/basis, but unfortunately they did not provide any details about their optimized structure. They also examined two-water clusters but apparently did not investigate cyclic structures. No previous work has performed a systematic study of trends across all four species microsolvated with up to three water molecules.

Lahsen *et al.*[7] recently reported work in which they computed the free energy curve of Li−F at the HF level with the perturbative reaction field approach. Although this is a promising technique, the use of a continuum reaction field may neglect important quantum mechanical effects that can only be treated by explicitly including the water molecules of the first solvation shell. This approach to modeling solvation also suffers from other difficulties, such as the lack of a definitive means for selecting the shape of the cavity.

The transition from cluster to solution can also be made by performing molecular dynamics simulations using interaction potentials parameterized either to reproduce bulk measured properties or to match *ab initio* results. Although accurate *ab initio* potentials should reproduce bulk solution behavior if all of the important many-body forces, nonlinear electrical responses, etc. are incorporated into the simulation, in practice this rarely occurs. More often than not, potentials parameterized for the bulk do not adequately describe clusters; binding energies and bond lengths cannot be predicted reliably. This inconsistency indicates that important many-body effects are not being adequately incorporated into the semiempirical potentials—that their success in bulk simulations is either a result of judicious cancellation of errors or some as yet unknown averaging of many-body effects that is not appropriate for the clusters. There is a clear need, therefore, for researchers using *ab initio* and molecular dynamics techniques to collaborate in order to resolve these issues.

Smith and Dang[2] have recently reported simulation results for NaCl in solution. Their best model used a polarizable potential for water,[8] i.e., the effective charge distribution of each water molecule is modified continuously in an iterative, self-consistent fashion in response to the current electrostatic fields of its neighbors. Lennard-Jones parameters for pair interactions between the ions and water were fit to reproduce gas-phase binding enthalpies. They computed the PMF and found minima at about 3 Å (CIP) and 5 Å (SSIP).

On the experimental side, Ault[9] measured the infrared spectra of argon matrix-isolated complexes of water and alkali halides, including LiCl and NaCl. He reported a shifted $^7LiCl$ anharmonic frequency of 518 $cm^{-1}$. For NaCl, he assigned a peak at 258 $cm^{-1}$ to the NaCl stretching frequency in the $NaCl(H_2O)$ complex. Unfortunately, the presence of the argon matrix hinders a direct comparison between Ault's values and those in the present work. Some of his conclusions regarding the structure of $NaCl(H_2O)$ are contradicted by the present calculations, although agreement for the frequency shift in LiCl is actually very good. It is possible that Ar⋯MX and $Ar\cdots H_2O$ interactions may alter the MX−water interaction to an extent which makes a direct comparison dubious.

In this work we have examined clusters with one to three waters for LiF and LiCl and one and two waters for NaF and NaCl. Beyond a comparison of variations in structures and energetics, we have also investigated the shifts in harmonic frequencies for intramolecular vibrations upon solvation and the effect of zero-point energy contributions. It is also important to consider the impact of basis set superposition error on the $MX-H_2O$ binding energies and the cluster structures. This has been carried out for the one-water clusters by completely reoptimizing all degrees of freedom on the counterpoise-corrected surface. Finally, we have studied some aspects of the asymptotic dissociation of the clusters to ionic products.

## Methodology

The correlation consistent basis sets of Dunning and co-workers[10] were used in this work. Sets of aug-cc-pVDZ quality were employed

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(8) Dang, L. X. *J. Chem. Phys.* **1992**, *97*, 2659.

(9) (a) Ault, B. S. *J. Phys. Chem.* **1975**, *79*, 621. (b) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.

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for F, Cl, O, and H.[11] The diffuse functions in the augmented sets are very important for describing the anionic character of $F^-$ and $Cl^-$, as well as for modeling the properties of water.[12] For Li and Na, cc-pVDZ sets were used.[13] These compact cationic species do not require extra diffuse functions.

Second-order Møller-Plesset perturbation theory (MP2) calculations were performed using either the MOLPRO92 suite of programs[14] or GAUSSIAN92.[15] Only valence electrons have been correlated, and only the five spherical contractions of the six Cartesian *d* functions have been used. The full Boys and Bernardi counterpoise (CP) correction[16] was used in those calculations where the effect of basis set superposition error (BSSE) was investigated.

Two calibration calculations were performed for LiF with one water to ascertain the magnitude of the errors introduced by using relatively small basis sets and MP2 theory. The $LiF(H_2O)$ cluster was first optimized (with no correction for BSSE) using the MP2 method and aug-cc-pVTZ sets on F, O, and H and the cc-pVTZ set on Li (MP2/VTZ). Secondly, an optimization was carried out with double zeta quality sets and the CCSD(T) method[17] [CCSD(T)/VDZ]. The association energy of $LiF(H_2O)$ is 20.26 kcal/mol at the MP2/VDZ level (see next section for more detail). Improving the level of theory to CCSD(T)/VDZ increases the binding energy by only 0.18 kcal/mol to 20.44 kcal/mol. Improving the basis set to triple zeta quality (MP2/VTZ) slightly reduces the binding energy by 0.41 kcal/mol to 19.85 kcal/mol. The changes are small and tend to partially cancel one another. Changes in structure are also small. The sufficiency of using MP2 theory with double zeta quality basis sets has been previously observed for the corresponding ion−water interactions,[18] and these calibration calculations demonstrate that MP2/VDZ is also sufficient for the present study.

## Results and Discussion

**1. Geometries and Energetics of Cyclic $MX(H_2O)_n$ Minima.** The geometric parameters used for the cluster calculations are depicted in Figure 2. The $C_1$ structure (**1**) for the one-water case is shown, but the same parameters were used for the larger clusters as well. The optimum structure for all four alkali halides is cyclic, with M, X, O, and H1 forming a nearly planar four-membered ring. H2 is bent out of plane by 20° to 45° depending on the MX species involved. A cyclic structure allows the water molecule to act as both donor and acceptor simultaneously. Other structures in which the water interacts with only the metal or the halide either lead to higher energy local minima or collapse to the cyclic structure (see topic 2 below).

The $C_2$ structure for MX with two water molecules simply places the second water such that it is rotated 180° around the MX axis from the first water (structure **5** in Figure 3), and the $C_3$ structure for three waters likewise locates the second and third waters ±120° away from the first water (structure **6** in Figure 3). Therefore, only nine parameters need to be optimized for any of the clusters. In the one and two water clusters all nine parameters were optimized simultaneously, while in the $LiX(H_2O)_3$ clusters the water bond angle $\theta$ and the $r$(OH2) bond length were optimized in a pass between separate minimizations over the seven other parameters.

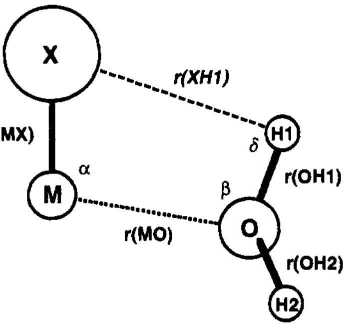
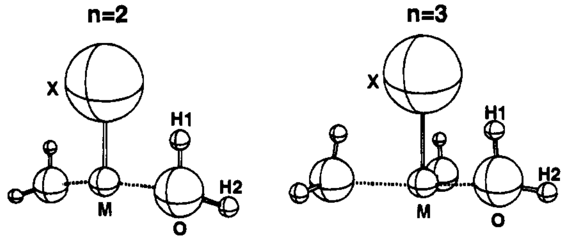


**Figure 2.** Geometrical parameters for cyclic $MX(H_2O)_n$ clusters (**1**). Nine parameters were optimized. Shown in the figure are the bond lengths r(MX), r(MO), r(OH1), and r(OH2); the bond angles X−M−O ($\alpha$) and M−O−H1 ($\beta$). Not indicated are the water bond angle H1−O−H2 ($\theta$) or the torsional angles X−M−O−H1 ($\gamma$) and X−H1−O−H2 ($\phi$). Two other parameters that are of interest, the r(XH1) bond length and X−H1−O bond angle ($\delta$), are determined by those which are explicitly optimized.



**5** **6**

**Figure 3.** Structures for $C_2$ $MX(H_2O)_2$ (**5**) and $C_3$ $MX(H_2O)_3$ (**6**) clusters.

Table 1 lists the total energies, aggregation energies, and geometrical parameters for the $MX(H_2O)$ clusters with no correction for basis set superposition error (BSSE). The aggregation energies are simply the $\Delta E_e$'s for the reaction

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

i.e.,

$$\Delta E_{n-1,n} = \Delta E_n - \Delta E_{n-1}$$

They are the incremental energy lowerings upon adding a water molecule to the cluster with one fewer waters. For $n = 1$ the aggregation energies are very similar, with a spread of only slightly more than 4 kcal/mol. This is true in spite of the fact that the $M^+(H_2O)$ and $X^-(H_2O)$ interaction energies vary from −32.9 kcal/mol [$Li^+(H_2O)$] to −14.7 kcal/mol [$Cl^-(H_2O)$].[18] This trend continues when the second water is added. Furthermore, the incremental changes in the aggregation energy do not substantially change when the second water is added to any of the MX species. The variation ranges from −0.7 kcal/mol in NaCl to +1.4 kcal/mol in NaF. Adding water to $NaF(H_2O)$ to form $NaF(H_2O)_2$ is the only instance in which the addition of water actually increases the incremental binding energy. The incremental energy lowerings for adding the third water to LiF

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[11] Primitive and contracted basis set sizes: H, (5s 2p)/[3s 2p]; O, F (10s 5p 2d)/[4s 3p 2d]; and Cl (13s 9p 2d)/[5s 4p 2d].

[12] Feller, D. *J. Chem. Phys.* **1993**, *98*, 7059.

[13] Primitive and contracted basis set sizes: Li (9s 4p 1d)/[3s 2p 1d]; Na (12s 9p 1d)/[4s 3p 1d].

[14] MOLPRO92 is a suite of programs written by H. -J. Werner and P. J. Knowles with contributions by J. Almlöf, R. D. Amos, M. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, E.-A. Reinsch, A. J. Stone, and P. R. Taylor.

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[18] Results for $F^-(H_2O)$ and $Cl^-(H_2O)$ from Xantheas, S. S. *8th American Conference on Theoretical Chemistry*; University of Rochester: Rochester, NY, 1993. Results for $Li^+(H_2O)$ from Feller, D.; Glendening, E. D.; Kendall, R. A.; Peterson, K. A., *J. Chem. Phys.*, **1994**, *100*, 4981. Results for $Na^+(H_2O)$ from Feller, D.; Glendening, E. D.; Woon, D. E. Unpublished.

**Table 1.** Total energies, Aggregation Energies, and Geometric Parameters for $MX(H_2O)_n$ Clusters Computed at the MP2 Level with cc-pVDZ/aug-cc-pVDZ Basis Sets[a]

| quantity | $n$ | $LiF(H_2O)_n$ | $LiCl(H_2O)_n$ | $NaF(H_2O)_n$ | $NaCl(H_2O)_n$ |
|---|---|---|---|---|---|
| $E$ | 0 | −107.185 87 | −467.195 60 | −261.571 79 | −621.596 53 |
| | 1 | −183.479 06 | −543.488 70 | −337.867 62 | −697.885 32 |
| | 2 | −259.770 61 | −619.779 91 | −414.165 39 | −774.173 08 |
| | 3 | −336.058 35 | −696.067 78 | | |
| $\Delta E$ | 1 | −20.3 | −20.2 | −21.9 | −17.5 |
| | 2 | −19.2 | −19.0 | −23.1 | −16.8 |
| | 3 | −16.8 | −16.9 | | |
| $r(MX)^b$ | 0 | 1.611 | 2.088 | 1.990 | 2.426 |
| | 1 | 1.686 | 2.151 | 2.098 | 2.511 |
| | 2 | 1.780 | 2.246 | 2.253 | 2.630 |
| | 3 | 1.953 | 2.440 | | |
| $r(MO)^b$ | 1 | 1.965 | 1.941 | 2.299 | 2.315 |
| | 2 | 1.977 | 1.963 | 2.307 | 2.326 |
| | 3 | 2.004 | 1.990 | | |
| $r(OH1)^b$ | 1 | 1.001 | 0.980 | 1.022 | 0.988 |
| | 2 | 0.994 | 0.980 | 1.006 | 0.988 |
| | 3 | 0.992 | 0.982 | | |
| $r(OH2)^b$ | 1 | 0.963 | 0.965 | 0.962 | 0.964 |
| | 2 | 0.963 | 0.965 | 0.962 | 0.964 |
| | 3 | 0.964 | 0.965 | | |
| $r(XH1)$ | 1 | 1.671 | 2.442 | 1.522 | 2.227 |
| | 2 | 1.710 | 2.355 | 1.586 | 2.239 |
| | 3 | 1.709 | 2.300 | | |
| $\alpha^b$ | 1 | 85.6 | 97.5 | 68.1 | 78.5 |
| | 2 | 84.0 | 93.8 | 66.8 | 76.5 |
| | 3 | 79.9 | 86.9 | | |
| $\beta^b$ | 1 | 70.3 | 85.9 | 69.3 | 81.1 |
| | 2 | 73.1 | 85.9 | 73.7 | 82.8 |
| | 3 | 75.2 | 85.4 | | |
| $\gamma^b$ | 1 | 2.4 | 2.4 | 1.2 | 1.3 |
| | 2 | 2.7 | 2.3 | 1.3 | 1.3 |
| | 3 | 3.2 | 2.0 | | |
| $\phi^b$ | 1 | 42.2 | 37.1 | 24.9 | 22.9 |
| | 2 | 42.4 | 40.2 | 23.1 | 24.0 |
| | 3 | 47.9 | 49.4 | | |
| $\theta^b$ | 1 | 107.3 | 106.5 | 107.5 | 106.3 |
| | 2 | 106.3 | 106.2 | | |
| $\delta$ | 1 | 135.8 | 122.2 | 151.2 | 140.7 |
| | 2 | 135.5 | 125.8 | 150.4 | 142.0 |
| | 3 | 139.0 | 133.9 | | |

[a] Total energies are in hartrees, energy differences are in kcal/mol, bond lengths are in Å, and angles are in degrees. See Figure 2 for identification of parameters. Isolated water parameters are: $E = -76.260\,91\ E_h$, r(OH) = 0.966 Å, and $\theta = 103.9°$. [b] Optimized parameters.

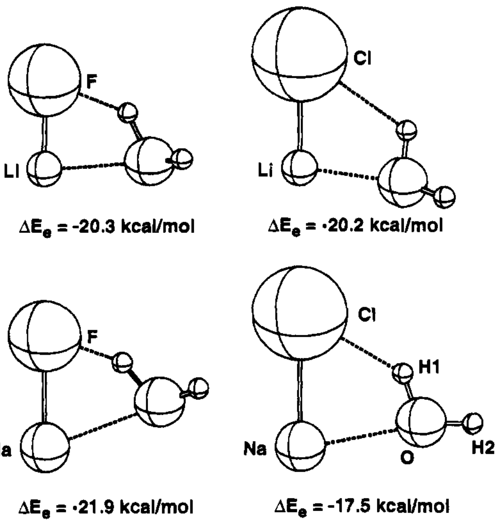

**Figure 4.** Cyclic $MX(H_2O)$ structures and binding energies for LiF, LiCl, NaF, and NaCl. Although all four clusters are very similar, the relative position of the water molecule reflects the relative strengths of the $X^-{-}H_2O$ and $M^+{-}H_2O$ pair interactions (see text).

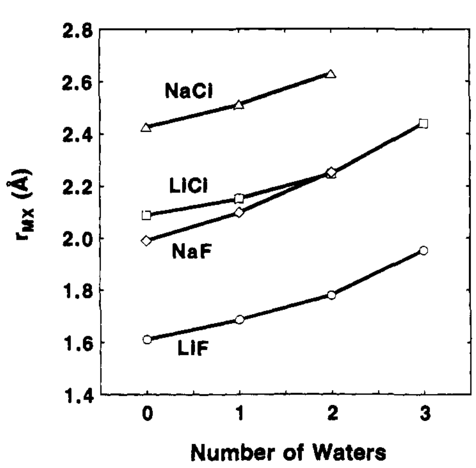

**Figure 5.** MX bond length $r(MX)$ (in Å) as a function of the number of waters in the cluster for LiF (○), LiCl (□), NaF (◇), and NaCl (△).

and LiCl are again very similar and approximately 2 kcal/mol less than the lowerings from the addition of the second water molecule.

The calculated optimum geometries for $MX(H_2O)$ are depicted in Figure 4. Although similarities in the structures are apparent, the differences clearly reflect the relative strengths of the $Li^+(H_2O)$, $Na^+(H_2O)$, $F^-(H_2O)$, and $Cl^-(H_2O)$ interactions, which are −32.9, −22.2, −26.9, and −14.7 kcal/mol, respectively.[18] For example, in $LiCl(H_2O)$ the $Li^+(H_2O)$ interaction is much stronger than the $Cl-(H_2O)$ interaction, and thus the Cl−H1−O bond angle ($\delta$) of 122.2° is substantially distorted from the roughly linear geometry of the ion−water interaction [167.9° in $Cl^-(H_2O)$]. In contrast, for $NaF(H_2O)$ the bond angle $\delta$ is 151.2°, substantially closer to the 176.9° found in $F^-(H_2O)$.

Consider also the bond lengths. The respective $M^+{-}O$ bond lengths in $Li^+(H_2O)$ and $Na^+(H_2O)$ are 1.879 and 2.238 Å. The $X^-{-}H$ bond lengths in $F^-(H_2O)$ and $Cl^-(H_2O)$ are 1.414 and 2.159 Å, respectively. For the two $LiX(H_2O)$ species, the $Li^+{-}O$ distances are about 0.06 and 0.09 Å longer than those for the $Li^+$−water species. For $NaX(H_2O)$, the distances lengthen by similar amounts. The differences tend to be much greater for the $X^-{-}H$ distance. In $LiF(H_2O)$ and $LiCl(H_2O)$, $r(XH)$ is 0.26 and 0.28 Å longer, respectively, than in the $X^-$−water clusters. The interaction with $Li^+$ dominates the geometry. In $NaF(H_2O)$ and $NaCl(H_2O)$ the differences are substantially reduced: the $X^-{-}H$ distances are only 0.11 and 0.07 Å longer than those for the respective $X^-$−water clusters.

Perhaps the most intriguing trend exhibited by the data is the change in the MX bond lengths as successive water molecules are added to the clusters. Figure 5 shows the bond lengths as a function of the number of added water molecules. Pronounced relaxation occurs with even one water. The changes for the two $LiX(H_2O)$ clusters are 0.075 Å (LiF) and 0.063 Å (LiCl), while the increases in the $NaX(H_2O)$ clusters are 0.108 Å (NaF) and 0.085 Å (NaCl). Moreover, the effect becomes *more* pronounced with the addition of each successive water molecule. In LiF the first water lengthens the bond by 0.075 Å, the second water by 0.094 Å, and the third water by 0.173 Å. The net change is 0.342 Å. Similar changes are observed in the other three alkali halides as well. It is evident that only a small quantity of water causes a substantial increase in the separations between the ions. Interestingly enough, the MX bond length in $NaCl(H_2O)_2$ has increased to 2.630 Å. Using the LiX cases as an example, the change due to adding the third water to NaCl will likely be larger than the change of 0.12 Å

**Table 2.** Energetic and Geometric Parameters for $MX(H_2O)$ Clusters Computed at the MP2 Level with Double Zeta Quality Sets with and without the Counterpoise Correction (CPC) for BSSE[a]

| quantity | CPC? | $LiF(H_2O)$ | $LiCl(H_2O)$ | $NaF(H_2O)$ | $NaCl(H_2O)$ |
|---|---|---|---|---|---|
| $\Delta E$ | N | −20.3 | −20.2 | −21.9 | −17.5 |
| | Y | −18.6 | −18.8 | −20.3 | −16.4 |
| $r(MX)^b$ | N | 1.686 | 2.151 | 2.098 | 2.511 |
| | Y | 1.683 | 2.155 | 2.089 | 2.508 |
| $r(MO)^b$ | N | 1.965 | 1.941 | 2.299 | 2.315 |
| | Y | 1.981 | 1.950 | 2.314 | 2.318 |
| $r(OH1)^b$ | N | 1.001 | 0.980 | 1.022 | 0.988 |
| | Y | 0.996 | 0.978 | 1.016 | 0.986 |
| $r(OH2)^b$ | N | 0.963 | 0.965 | 0.962 | 0.964 |
| | Y | 0.964 | 0.965 | 0.962 | 0.964 |
| $r(XH1)$ | N | 1.671 | 2.442 | 1.522 | 2.227 |
| | Y | 1.736 | 2.538 | 1.567 | 2.277 |
| $\alpha^b$ | N | 85.6 | 97.5 | 68.1 | 78.5 |
| | Y | 86.9 | 99.4 | 68.9 | 79.5 |
| $\beta^b$ | N | 70.3 | 85.9 | 69.3 | 81.1 |
| | Y | 71.4 | 87.8 | 69.8 | 82.1 |
| $\gamma^b$ | N | 2.4 | 2.4 | 1.2 | 1.3 |
| | Y | 2.4 | 2.3 | 1.1 | 1.1 |
| $\phi^b$ | N | 42.2 | 37.1 | 24.9 | 22.9 |
| | Y | 43.2 | 37.2 | 26.1 | 20.1 |
| $\theta^b$ | N | 107.3 | 106.5 | 107.5 | 106.3 |
| | Y | 107.0 | 106.3 | 107.4 | 106.4 |
| $\delta$ | N | 135.8 | 122.2 | 151.2 | 140.7 |
| | Y | 133.6 | 119.1 | 149.6 | 138.8 |

[a] Total energies are in hartrees, energy differences are in kcal/mol, bond lengths are in Å, and angles are in degrees. [b] Optimized parameter.

observed upon adding the second water. Thus, the NaCl distance in $NaCl(H_2O)_3$ is expected to approach the distance of 3 Å found for the contact ion pair in the simulations of Smith and Dang.[2]

Harmonic frequencies and zero-point energies were computed for the $MX(H_2O)$ and $MX(H_2O)_2$ clusters, and all were verified to be true minima. Discussion of the frequencies merits a section of its own (see section 4 below). Zero-point corrections for the one and two water complexes, respectively, are (in kcal/mol) as follows: LiF (1.2, 3.5); LiCl (1.1, 3.4); NaF (1.9, 4.1); NaCl (1.9, 3.7). Zero-point energy has little effect upon the trends discussed above.

**2. Correction for Basis Set Superposition Errors in MX-($H_2O$).** Table 2 compares the uncorrected energies and geometrical parameters for $MX(H_2O)$ with counterpoise-corrected results. These clusters provide a rare chance to look at BSSE in systems where cyclic intermolecular structures are involved. Full optimizations over all nine degrees of freedom were carried out on the CP-corrected surface. A correction for deformation was applied in the calculation of the binding energies, which are reduced by 1.1 to 1.7 kcal/mol with the counterpoise correction.

As is typical in instances where the entire structure is optimized on the CP-corrected surface, changes in the intramolecular degrees of freedom (the MX and OH bond lengths) are very small, generally 0.005 Å or less. The intermolecular distances $r(MO)$ and $r(XH1)$, however, lengthen significantly, especially the X−H1 distance. The former, $r(MO)$, changes by LiF (0.016 Å), LiCl (0.009 Å), NaF (0.015 Å), and NaCl (0.003 Å), which are relatively small adjustments. The distance between the halide ion and the nearest hydrogen, $r(XH1)$, on the other hand, changes by the following: LiF, 0.065 Å; LiCl, 0.096 Å; NaF, 0.045 Å; NaCl, 0.050 Å. The change in LiCl-($H_2O$) is particularly large. The most likely source of BSSE here lies in the description of the lone pairs on oxygen or the halides. The compact functions on the alkali metals have little to offer for the improvement of the oxygen charge distribution, and consequently there is only a small change in $r(MO)$ when the CP correction is applied. However, the halide ion evidently makes substantial use of the functions on H1 and hence the X−H1 distance lengthens appreciably when the correction is included. The effect is larger in $Cl^-$ than in $F^-$. The changes in $r(XH1)$ are similar to changes observed in $(H_2O)_2$ and $(HF)_2$.[19,20]

Intermolecular angles tend to change little when the CP correction is applied in systems without cyclic contact. Here, the torsion angle $\gamma$ is essentially unaffected, but the angles $\alpha$, $\beta$, and $\delta$, which are the internal angles of the quasiplanar X−M−O−H1 ring, shift by amounts which vary up to 3°. The largest change is again exhibited by $LiCl(H_2O)$.

**3. Other Possible Minimum Energy Structures for MX-($H_2O$).** For $MX(H_2O)$, we explored other geometries in search of alternative minima and saddle points. In particular, although the present work identifies the cyclic structure discussed above as the global minimum, one might also expect the possibility of local minima related to the $M^+(H_2O)$ or $X^-(H_2O)$ structures. For the latter case, the best candidate of the four MX species considered in this work is $NaF(H_2O)$, based on the relative strengths of the cation−water and anion−water interactions. However, an "anionic" minimum resembling structure **3** could not be located; any initial structure chosen to favor water interacting predominantly with the $F^-$ end of NaF collapsed into the $C_1$ cyclic minimum. The same trend was observed for $LiF(H_2O)$ and is assumed to be the case for the other two alkali halides.

However, all four $MX(H_2O)$ complexes form a $C_{2v}$ "cationic" minimum (structure **2**) in which the O, M, and X are collinear. This configuration, or one in which the water is bent slightly out of plane, is the one which has been identified as the global minimum in most previous *ab initio* work.[2−4] The cyclic structure appears to be favored only when sufficient diffuse functions have been added to the halides to describe their strong anionic character. Diffuse functions are also important for properly describing the electrostatic properties of water, which tend to be overestimated otherwise (especially with the HF wave function).

The uncorrected equilibrium interaction energies for the $C_{2v}$ minima for the $MX(H_2O)$ complexes with LiF, LiCl, NaF, and NaCl are −17.3, −19.1, −11.7, and −12.9 kcal/mol, respectively. Given the energies in Table 1, these minima therefore lie 3.0 (LiF), 1.1 (LiCl), 10.2 (NaF), and 4.6 (NaCl) kcal/mol above the cyclic minima. This trend is exactly what one would expect based on the relative energies for $Li^+$, $Na^+$, $F^-$, and $Cl^-$ interacting with a single water molecule: the second minimum lies closest to the global minimum for LiCl and farthest away for NaF.

Harmonic frequencies were computed for each of the optimized $C_{2v}$ structures in order to verify that they were true minima. Although the frequencies were all found to be positive, in every case the two smallest eigenvalues were found to be unusually small (~20−60 $cm^{-1}$), especially for the two NaX species. Given the wave function/basis set limitations, numerical uncertainties, and expected large anharmonic corrections, we can only tentatively identify these $C_{2v}$ structures as minima. The normal modes corresponding to the two lowest frequencies either bend the water molecule out of the plane or rotate it in the plane. In both instances, the motion moves one or both H atoms toward the halide end of the MX moiety.

The M−O distances for the four $C_{2v}$ minima are all somewhat longer than in $Li^+(H_2O)$ or $Na^+(H_2O)$. There are two contribu-

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(19) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104. Xantheas, S. S.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 8774.

(20) Peterson, K. A.; Dunning, T. H., Jr. In preparation.

tions to this effect: (1) the charge on $M^+$ in MX is slightly less than unity; i.e., charge transfer to the halide ion is incomplete, and therefore, charge−dipole and higher order interactions are reduced relative to $M^+(H_2O)$; (2) the negative charge on the halide interacts repulsively with the dipole moment of $H_2O$ in this alignment. The changes with respect to values for the ions[16] are as follows: LiF, +0.006 Å; LiCl, +0.008 Å; NaF, +0.159 Å; NaCl +0.084 Å. The shift is nearly negligible for the LiX cases but is at least an order of magnitude larger for NaX. This is consistent with the observed ionicities of the MX species.

**4. Transition States (TS) for Interconversion of Cyclic Minima in MX($H_2O$).** Structure **4** is the transition state between two symmetric cyclic MX($H_2O$) minima where the out-of-plane hydrogen (H2) lies on one side or the other of the quasiplanar ring comprised of the other four atoms. If the barrier for interconverison is not too large, one might consider the measurement of quantum tunneling as in $(H_2O)_3$ (ref 21) and other species. In fact, the calculations indicate that the out-of-plane hydrogen is extremely labile. The equilibrium energies are very similar (minimum vs transition state, in kcal/mol): LiF, −20.26/−19.79; LiCl −20.19/−19.99; NaF, −21.91/−21.86; NaCl, −17.50/−17.46. For all four species, there is little energy to be gained by rotating H2 out of plane, especially for NaF and NaCl, where the energy difference between minimum and transition state is less that 0.1 kcal/mol. Zero-point corrections further blur the distinction between minima and transition state. The zero-point corrections and imaginary frequencies are (in kcal/mol, $cm^{-1}$) LiF (0.71, 230i), LiCl (0.98, 175i), NaF (1.70, 120i), and NaCl (1.65, 102i). Thus, the values of $\Delta E_0$ are (minimum vs transition state, in kcal/mol) as follows: LiF, −19.11/−19.08; LiCl, −19.06/−19.01; NaF −19.97/−20.16; NaCl, −15.65/−15.81. In LiF and LiCl, the minima and TS are essentially isoenergetic, while in NaF and NaCl structure **4** is actually about 0.2 kcal/mol *lower* in energy than the $C_1$ geometry **1**. Changes in the frequencies of two normal modes account for the smaller zero-point energies of the transition state. The first one corresponds to the imaginary frequency, and the second is the one which H1 moves out of the plane. These are the only two modes that break the $C_s$ symmetry of the TS. Given the unusual energetics of the minima vs TS, H2 clearly possesses a great deal of freedom to flop above and below the plane defined by the other nuclei.

**5. Harmonic Frequencies for Global Minima in MX, MX($H_2O$), and MX$(H_2O)_2$.** The harmonic frequencies for the MX, MX($H_2O$), and MX$(H_2O)_2$ clusters confirm the trends that have been discussed above and reveal further interesting behavior. Table 3 lists selected frequencies for each of the MX($H_2O$) and MX$(H_2O)_2$ complexes. We have chosen to focus attention upon the effect of microsolvation on the frequencies that are dominated by the MX, OH1, and OH2 stretching motions.

The first trend to consider is the shift in the MX stretch as a function of the number of water molecules in the cluster. In general, the frequency shifts rapidly to lower values as water molecules are added to the clusters (i.e., reflecting the inverse behavior depicted in Figure 5). Adding one water reduces the frequency by an amount ranging from 127 $cm^{-1}$ in the case of LiCl to 225 $cm^{-1}$ for NaCl. The second water lowers the frequency by another 36 to 137 $cm^{-1}$ (see below, however). The calculated harmonic frequency for LiCl($H_2O$) of 516 $cm^{-1}$ is fortuitously close to Ault's[8] measured value of 518 $cm^{-1}$ considering that no correction for anharmonicity is included in the present work. His frequency of 258 $cm^{-1}$ for NaCl($H_2O$), however, is much smaller than our value of 311 $cm^{-1}$. If a direct comparison is valid, then it is possible that he saw NaCl$(H_2O)_2$, where we find an MX stretching frequency of 275 $cm^{-1}$. On the other hand, anharmonicity effects and/or the limitations of MP2 theory with relatively small sets could account for the difference. This, of course, assumes that the minimum energy structures and frequencies are little affected by the rare gas matrix. Ault[9] argues for a structure very different from the cyclic structure which we find to be the most stable structure in the gas phase.

**Table 3.** Harmonic Frequencies ($cm^{-1}$) Computed for MX($H_2O$) and MX$(H_2O)_2$ Clusters Using MP2 Theory and Double Zeta Quality Basis Sets[a]

| | LiF$(H_2O)_n$ | | LiCl$(H_2O)_n$ | |
|---|---|---|---|---|
| type | $n = 1$ | $n = 2$ | $n = 1$ | $n = 2$ |
| MX stretch | 711 | 577 | 516 | 379 |
| OH1 stretch | 3226 | 3326 | 3607 | 3600 |
| | | 3376 | | 3612 |
| OH2 stretch | 3906 | 3905 | 3899 | 3895 |
| | | 3906 | | 3896 |

| | NaF$(H_2O)_n$ | | NaCl$(H_2O)_n$ | |
|---|---|---|---|---|
| type | $n = 1$ | $n = 2$ | $n = 1$ | $n = 2$ |
| MX stretch | 474 | 414 | 311 | 275 |
| OH1 stretch | 2848 | 3065 | 3448 | 3483 |
| | | 3191 | | 3507 |
| OH2 stretch | 3923 | 3922 | 3906 | 3906 |
| | | 3923 | | 3906 |

[a] The frequencies of the isolated alkali halides with the same treatment are: LiF, 910; LiCl, 643; NaF, 366; and NaCl, 536. The frequencies for free water are 1622 (bend), 3803 (symmetric stretch), and 3937 (asymmetric stretch) $cm^{-1}$.

The one exception to the above trend is NaF, where the frequency *increases* by over 100 $cm^{-1}$ with the addition of one water and only starts to drop when the second water is added (though it remains larger than the gas-phase value). The MX bond length in NaF$(H_2O)_n$ clusters increases in the same manner and to a similar degree as in the other species, but the usual red shift does not occur. In order to understand this, it is useful to examine the associated normal mode in NaF($H_2O$) and contrast it with those of the other three one-water complexes. The couplings to other motions for the latter are very similar: the water rocks out of plane and the HOH angle bends as well. In contrast, the NaF motion is coupled to a water breathing mode with little rotation in NaF($H_2O$). Thus, the modes happen to be quite different in the various MX($H_2O$) clusters. NaF is the only case where the $X^-{-}H_2O$ interaction is comparable to or stronger than $M^+{-}H_2O$. The resulting normal mode appears to be analogous to the constrained motion one observes in ring structures. At the same time, there is also greater sensitivity in $X^-{-}H_2O$ interactions to changes in orientation. The bending modes[18] in $X^-(H_2O)$ are of higher energy than those of $M^+(H_2O)$, which reflect the importance in the former of charge transfer and its sensitivity to orbital overlap.

The stretching frequencies for water show two trends. The OH2 stretches in the MX$(H_2O)_n$ complexes are relatively insensitive to the number of water molecules and change little from the symmetric and asymmetric stretching frequencies of isolated water. H2 is directed away from the alkali halide and is unaffected by its presence or that of a second water. However, the OH1 frequency is very sensitive to the strength of the interaction with the MX fragment and, in particular, to the strength of the $X^-(H_2O)$ interaction. In LiCl($H_2O$) the frequency drops by about 200 $cm^{-1}$ relative to isolated water, but in NaF($H_2O$) it decreases by nearly 1000 $cm^{-1}$. The other two cases lie between these extremes. When two water molecules are present, the two related frequencies tend to

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(21) Pugliano, N.; Saykally, R. J. *Science* **1993**, *257*, 1937.

**Table 4.** Natural Charges for $MX(H_2O)_n$ Clusters Computed at the RHF Level with Double Zeta Quality Sets at the Uncorrected MP2 Geometries[a]

| MX | n | M | X | O | H1 | H2 |
|---|---|---|---|---|---|---|
| LiF | 0 | 0.984 | −0.984 | | | |
| | 1 | 0.977 | −0.945 | −1.094 | 0.560 | 0.502 |
| | 2 | 0.960 | −0.925 | −1.077 | 0.558 | 0.502 |
| | 3 | 0.939 | −0.900 | −1.064 | 0.552 | 0.499 |
| LiCl | 0 | 0.957 | −0.957 | | | |
| | 1 | 0.945 | −0.940 | −1.061 | 0.542 | 0.513 |
| | 2 | 0.928 | −0.929 | −1.050 | 0.541 | 0.510 |
| | 3 | 0.915 | −0.904 | −1.046 | 0.537 | 0.505 |
| NaF | 0 | 0.994 | −0.994 | | | |
| | 1 | 0.991 | −0.928 | −1.121 | 0.566 | 0.492 |
| | 2 | 0.986 | −0.901 | −1.102 | 0.563 | 0.496 |
| NaCl | 0 | 0.970 | −0.970 | | | |
| | 1 | 0.972 | −0.942 | −1.072 | 0.539 | 0.503 |
| | 2 | 0.972 | −0.923 | −1.065 | 0.538 | 0.503 |

[a] Partial charges for $H_2O$ in the gas phase are O (−0.967) and H (0.484).

increase slightly as the waters are pushed slightly farther away by steric repulsion.

**6. Partial Charges of Cyclic $MX(H_2O)_n$ Clusters.** A natural population analysis[22] (NPA) was performed with GAUSSIAN92[15] for each cyclic minimum structure using RHF density matrices. This is sufficient to identify trends. The natural partial charges are given in Table 4. The largest changes occur when the first water is added. For all four MX species, significant charge is transferred from the halide onto the water. Charge is also transferred from the H atoms onto the O atom as the water molecule is polarized by the ions. Adding additional water molecules has little effect on charge transfer between MX and the surrounding waters, though O tends to become less polarized. For the two Li halides, the metal charge decreases markedly as the number of waters increases. It is essentially unchanged for the Na cases.

**7. Search for an MOH−HX Structure.** If the MX distance in any of the one-water clusters is systematically stetched and the other geometrical parameters are reoptimized at each step, $MX(H_2O)$ dissociates into MOH + HX rather than into MX + $H_2O$ (see Figure 6 for $LiF(H_2O)$). This raised the question of a possible minimum corresponding to MOH−HX. Although we found no stable structure with this configuration, there is a shoulder where the slope of the "reaction path" changes significantly. This corresponds to the point where H1 migrates from $H_2O$ to X, forming distinct HX and MOH moieties. However, there appears to be no stationary point corresponding to a stable MOH−HX structure. The dissociated limits for HX + MOH products lie 18−40 kcal/mol above MX + $H_2O$.

**8. Asymptotic Behavior and the Ionic Channel: $MX(H_2O)_n \rightarrow M^+(H_2O)_m + X^-(H_2O)_{n-m}$.** For clusters containing up to three water molecules, the ionic exit channel lies at much higher energies than the asymptotes discussed previously. However, considering the asymptote that produces solvated ions is very important for comparing to solution simulations.

Figure 7 depicts the trends for the $LiCl(H_2O)_n$ complexes. The cost of breaking up LiCl and moving the ions to infinite separation is 148.5 kcal/mol (MP2/cc-pVDZ, aug-cc-pVDZ). If one water molecule is added to the complex, LiCl is stabilized by −20.2 kcal, but the products, $Li^+(H_2O)$+$Cl^-$, are stabilized by −32.9 kcal/mol. $Li^+(H_2O)$ + $Cl^-$ is the preferred product because the interaction between water and $Li^+$ is much stronger than that between water and $Cl^-$. Thus, the energy required to dissociate LiCl into hydrated ions has dropped to 135.9 kcal/mol. The second and third waters lower this further to 125.9 and 119.8 kcal/mol, respectively. The net change between zero and three waters is 28.7 kcal/mol. Although this is a rather dramatic change, in solution the contact ion pair is bound by only a few kcal/mol (see Smith and Dang[2]).

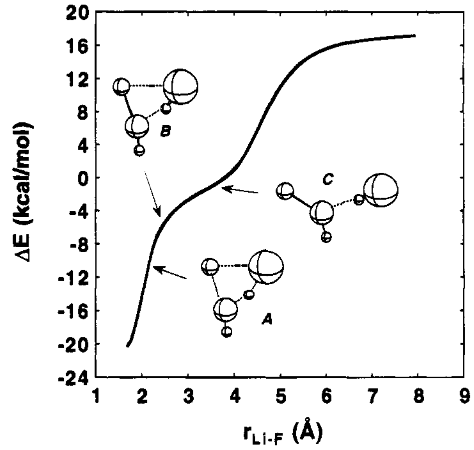

**Figure 6.** Dissociation of $LiF(H_2O) \rightarrow LiOH + HF$ determined by lengthening the LiF distance and reoptimizing all other geometric parameters. ΔE is referenced to the lowest energy products, LiF + $H_2O$. Two bonds are shifted: Li−F and O−H1 bonds become Li−O and H1−F bonds. At point A, H2 has moved into the plane. The Li−O and H1−F distances have contracted while Li−F and O−H1 have lengthed. H2 then migrates onto F (B). The LiOH(HF) complex (C) has no minimum and requires another 20 kcal/mol to dissociate.

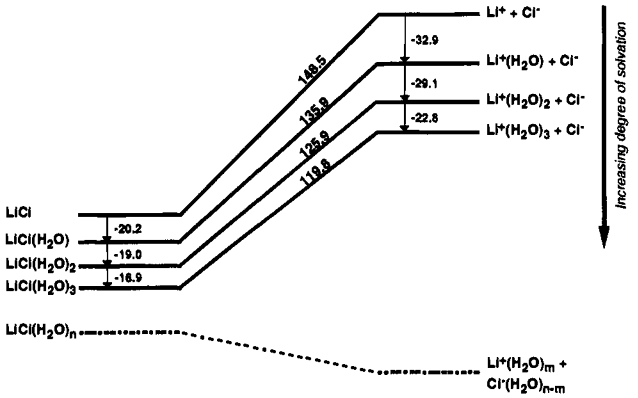

**Figure 7.** Equilibrium dissociation energy (in kcal/mol) of $LiCl(H_2O)_n \rightarrow Li^+(H_2O)_m + Cl^-(H_2O)_{n-m}$ for $n = 0$ to 3. When water is added to the gas-phase reactant LiCl and products $Li^+$ and $Cl^-$, the products are preferentially stabilized. Successive waters steadily decrease the dissociation energy of the complex. In the case of LiCl, the first three water molecules will all tend to solvate the cation since the binding of water to $Li^+$ is substantially favored over binding to $Cl^-$.

## Conclusions

The minimum energy structure for all of the $MX(H_2O)$ clusters was found to be cyclic, with the O atom oriented toward the metal atom and one of the hydrogen atoms oriented toward the halogen atom. The M−X−O−H atoms are essentially coplanar; the remaining hydrogen atom lies above (or below) this plane, although the barrier to inversion is very small. The details of the structure are largely determined by the strengths of the $M^+(H_2O)$ and $X^-(H_2O)$ interactions. Addition of a single water molecule had a dramatic effect on the MX bond, increasing the optimum bond length by 0.06−0.11 Å and decreasing the harmonic frequency by 130−225 $cm^{-1}$ (interest-

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[22] Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

ingly enough, addition of a single water molecule to NaF *increased* the frequency).

The optimum position for the second water molecule in the $MX(H_2O)_2$ clusters was rotated 180° around the MX bond relative to the first water molecule. Again, dramatic effects were observed for the MX bond: $\Delta r(MX) = 0.09-0.16$ Å and $\Delta\omega(MX) = 40-140$ cm$^{-1}$. Finally, addition of a third water molecule to the $LiX(H_2O)_2$ clusters increased the MX bond length by an additional 0.17−0.19 Å.

The energetics of dissociation to the $M^+ + X^-$ ion pair as a function of solvation was also considered. Addition of a single water molecule to LiCl decreased the dissociation energy by 12.7 kcal/mol (from 148.5 to 135.9 kcal/mol). For $LiCl(H_2O)_3 \rightarrow Li^+(H_2O)_3 + Cl^-$, the lowest dissociation limit for the alkali halide−water trimer, the calculated dissociation energy was just 119.8 kcal/mol. Although this is a rather dramatic change, it is far from that observed in solution, where the contact ion pair is bound by only a few kcal/mol.

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