Inorg. Chem. **2006**, *45*, 4811–4819

Inorganic Chemistry Article

Factors Governing the Metal Coordination Number in Isolated Group IA and IIA Metal Hydrates

Ingvar Tunell[†,§] **and Carmay Lim***[,†,‡]

Institute of Biomedical Sciences, Academia Sinica, Taipei 115, Taiwan, and Department of
Chemistry and the Department of Life Sciences, National Tsing Hua University,
Hsinchu 300, Taiwan

Received November 15, 2005

Many of the group IA and IIA metal ions, such as Na^+, K^+, Mg^{2+}, and Ca^{2+}, play crucial roles in biological functions. Previous theoretical studies generally focus on the number of water molecules bound to a particular (as opposed to all) alkali or alkaline earth cations and could not establish a single preferred CN for the heavier alkali and alkaline earth ion–water complexes. Crystal structures of hydrated Na^+, K^+, and Rb^+ also cannot establish the preferred number of inner-shell water molecules bound to these cations. Consequently, it is unclear if the gas-phase CNs of group IA metal hydrates increase with increasing ion size, as observed for the group IIA series from the Cambridge Structural Database, and if the same factors govern the gas-phase CNs of both group IA and IIA ion–water complexes. Thus, in this work, we determine the number of water molecules directly bound to the series of alkali (Li^+, Na^+, K^+, and Rb^+) and alkaline earth (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) metal ions in the gas phase by computing the free energy for forming an isolated metal–aqua complex as a function of the number of water molecules at 298 K. The preferred gas-phase CNs of group IA hydrates appear insensitive to the ion size; they are all 4, except for Rb^+, where a CN of 6 seems as likely. In contrast, the preferred gas-phase CNs of the group IIA dications increase with increasing ion size; they are 4 for Be^{2+}, 6 for Mg^{2+} and Ca^{2+}, and 7 for Sr^{2+} and Ba^{2+}. An entropic penalty disfavors a gas-phase CN greater than 4 for group IA hydrates, but it does not dictate the gas-phase CNs of group IIA hydrates. Instead, interactions between the metal ion and first-shell water molecules and between first-shell and second-shell water molecules govern the preferred gas-phase CNs of the group IIA metal hydrates.

1. Introduction

Nearly half of all proteins contain metal cofactors, which are essential to life. The metal's primary coordination number, referred to below as simply the CN, governs the three-dimensional structure and thus the properties and function of the metal complex. A recent Cambridge Structural Database (CSD) survey of the CNs of metal ions in the entire periodic table[1] showed that, as expected, the preferred CN increases with increasing size of the dication for the alkaline earth metal series. Surprisingly, however, it does not increase with increasing size of the monocation for the alkali metal series; high-resolution (R-factor < 5%) CSD complexes with all types of ligands show that the preferred CN is 6 for Na^+ but 4 for the smaller Li^+ and larger K^+, whereas complexes containing only water molecules show that the preferred CN is 4 for Li^+, indeterminate for Na^+, and uncertain for K^+.[1] Because many of the group IA and IIA cations are crucial for biological function, it would be of great interest to identify the factors determining the preferred CNs of these metal ions in the various phases (gas, crystalline, and solution). As a first step, our goals herein are (1) to determine the gas-phase CN of an isolated group IA/IIA metal−aqua complex, defined as the preferred number of water molecules coordinated to a group IA/IIA metal ion in the gas phase (i.e., in the absence of other interactions such as bulk solvent), and (2) to identify the factors governing the preferred gas-phase CNs of these metal hydrates.

Many theoretical studies of group IA and IIA cations, hydrated in the gas phase or in aqueous solution, have been performed,[2−12] mostly with the aim of investigating the

---

[*] To whom correspondence should be addressed. E-mail: carmay@gate.sinica.edu.tw.

[†] Academia Sinica.

[§] Department of Life Sciences, National Tsing Hua University.

[‡] Department of Chemistry, National Tsing Hua University.

(1) Dudev, M.; Wang, J.; Dudev, T.; Lim, C. *J. Phys. Chem. B* **2006**, *110*, 1889.

10.1021/ic0519741 CCC: $33.50 © 2006 American Chemical Society
Published on Web 05/09/2006

reliability of the calculations and/or reporting the structures, thermodynamic properties, and spectra of specific ions. For example, gas-phase binding energies and enthalpies of group IA[3] and group IIA[6,7] cations binding to water molecules have been computed with different methods with the goal of determining the theory level and basis set that can reliably describe the metal−water distances and energies. Although most of the ab initio studies report the lowest-energy structures for a given alkali/alkaline earth metal hydrate and the respective energies, a few studies have also computed the free energy for water molecules binding to a specific alkali or alkaline earth ion (rather than all group IA/IIA cations) in the gas phase at 298 K. A CN of 4 has been obtained for hydrated Li^+ in the gas phase from ab initio free-energy calculations[8,10] as well as in aqueous solution from quasichemical theory and ab initio molecular dynamics simulations.[10,11] From free energies computed at the MP2/TZ2P//HF/TZ2P level, researchers found no single preferred CN for hydrated Na^+, K^+, and Rb^+; the free energy of a Na^+ or Rb^+ bound to four water molecules is comparable to that of the respective metal ion bound directly to five water molecules,[4,12] whereas structures of K^+ bound to four, five, and six first-shell water molecules have comparable stabilities.[9] On the other hand, from free energies computed at the MP2/6-311++G**//RHF/6-31G* level, researchers have obtained CNs of 4 and 6 for hydrated Be^{2+} and Mg^{2+}, respectively.[5] None of the previous studies, to the best of our knowledge, have compared the preferred CNs of hydrated group IA ions with those of hydrated group IIA ions in the gas phase or determined the factors governing their preferred gas-phase CNs.

Despite the plethora of studies on the hydration of group IA and IIA cations, several important questions remain. For example, (1) what are the preferred gas-phase CNs of the bulkier alkali ions, Na^+, K^+, and Rb^+, in complexes with water molecules? (2) Do the gas-phase CNs of monovalent alkali metal hydrates increase with increasing size of the ion, as observed in the CSD for the divalent alkaline earth metal series (see above)? (3) What are the factors governing the preferred gas-phase CNs of group IA and IIA metal hydrates and are these factors the same? (4) What factors account for the observed changes in the preferred CNs of certain metal hydrates upon solvation? To address these questions, we first predict the preferred number of water molecules bound to the alkali monocations, Li^+, Na^+, K^+, and Rb^+, as well as the alkaline earth dications, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, in the gas phase by computing the free energy for the binding of n water molecules to each metal ion (Me^{+q}) of charge q at 298 K

$$Me^{+q} + n(H_2O) \rightarrow [Me(H_2O)_{n-m}\cdot(H_2O)_m]^{+q} \qquad (1)$$

In eq 1, the bullet separates the $n - m$ water molecules in the first shell from the m water molecules in the second shell. For a given metal hydrate, its preferred gas-phase CN corresponds to the minimum in the gas-phase free energy of reaction 1 as a function of n. The reliability of the structure and energy calculations was validated by comparing (i) the optimized geometries with the respective CSD structures, and (ii) the computed incremental free energies for the successive binding of a water molecule to the metal−aqua complex with the respective experimental values, where available.

This study adds to previous works by including both group IA and group IIA hydrates in order to evaluate the relative contributions of the enthalpic and entropic terms to the gas-phase free energy of eq 1 as a function of ion size and charge distribution. The results reveal that the preferred number of metal-bound water molecules in the gas phase is relatively insensitive to the size of the alkali monocation, but increases with increasing size of the alkaline earth dication. They also reveal the physical basis for these trends and the reason the preferred number of water molecules bound to a group IA monocation in the gas phase is not larger than that bound to the smaller group IIA counterpart.

2. Methods

Geometry Optimization. All geometries were optimized using the Gaussian 03 program[13] with the three-parameter hybrid method by Becke[14] in conjunction with the Lee, Yang, and Parr correlation functional,[15] B3-LYP, which has been shown to yield good overall performance from benchmark studies by Zhao and co-workers[16] and references therein. The geometries were optimized using the 6-31G** basis set[17−19] on all atoms except for the heavier metal ions, Rb^+, Sr^{2+}, and Ba^{2+}, which employed the SDD basis set.[20] The 6-31G** basis set was chosen because the B3-LYP/6-31G** optimized geometry of $[Mg (H_2O)_6]^{2+}$ and the respective B3-LYP/6-311++G(2df,2pd) and B3-LYP/6-311++G(3df,3pd) electronic energies are similar to those computed using the much larger 6-31++G** and 6-311++G(2df,2pd) basis sets (see the Supporting Information, Table S1). Correlation-consistent polarized type basis sets such as cc-pVTZ and their augmented counterparts were not considered, as they are not properly defined for several of the alkali

---

(2) Bock, C. W.; Glusker, J. P. *Inorg. Chem.* **1993**, *32*, 1242.
(3) Glendening, E. D.; Feller, D. *J. Phys. Chem.* **1995**, *99*, 3060.
(4) Kim, J.; Lee, S.; Seung, J. C.; Byung, J. M.; Kim, S. K. *J. Chem. Phys.* **1995**, *102*, 839.
(5) Markham, G. D.; Glusker, J. P.; Bock, C. L.; Trachtman, M.; Bock, C. W. *J. Phys. Chem.* **1996**, *100*, 3488.
(6) Glendening, E. D.; Feller, D. *J. Phys. Chem.* **1996**, *100*, 4790.
(7) Pavlov, M.; Siegbahn, P. E. M.; Sandström, M. *J. Phys. Chem. A* **1998**, *102*, 219.
(8) Tongraar, A.; Liedl, K. R.; Rode, B. M. *Chem. Phys. Lett.* **1998**, *286*, 56.
(9) Lee, M. L.; Kim, J.; Lee, S.; Byung, J. M.; Kim, S. K. *J. Chem. Phys.* **1999**, *111*, 3995.
(10) Rempe, S. B.; Pratt, L. R.; Hummer, G.; Kress, J. D.; Martin, L. M.; Redondo, A. *J. Am. Chem. Soc.* **2000**, *122*, 966.
(11) Lyubartsev, A. P.; Laasonen, K.; Laaksonen, A. *J. Chem. Phys.* **2001**, *114*, 3120.
(12) Park, J.; Kolaski, M.; Lee, H. M.; Kim, S. K. *J. Chem. Phys.* **2004**, *121*, 3108.
(13) Frisch, M. J.; et al. *Gaussian 03*, rev. B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.
(14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.
(16) Zhao, Y.; Pu, J.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 673.
(17) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(18) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A.; Gordon, M. S. *J. Chem. Phys.* **1982**, *77*, 3654.
(19) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys.* **1998**, *109*.
(20) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1991**, *94*, 1360.

Table 1. Comparison between Calculated (r_{calcd}) and Experimental (r_{expt}) Metal−O(water) Distances (Å) in Optimized Gas-Phase and Crystal Ion−Aqua Complexes

Me^{q+}	CN	r_{calcd}(Me−O)[a]	r_{expt}(Me−O)[b]
Li^+	4	1.946	1.922[c]
Na^+	4	2.269	2.224[d]
K^+	4	2.673	[e]
Rb^+	4	2.870	[e]
Be^{2+}	4	1.647	1.613−1.620[f]
Mg^{2+}	6	2.098	2.046−2.087[g]
Ca^{2+}	7	2.432−2.513	2.350−2.421[h]
Sr^{2+}	8	2.630	2.585−2.614[i]
Ba^{2+}	9	2.725−2.911	[e]

[a] Distances computed using B3-LYP with the SDD basis set for Rb^+, Sr^{2+}, and Ba^{2+} and the 6-31G** basis set for the other metal ions and water atoms. [b] Experimental values from CSD X-ray diffraction structures, with the lowest R-factor corresponding to the CN in the table.[1] [c] Taken from CSD entry COVBEU; R-factor = 2.6%. [d] Taken from CSD entry GIXBAQ; R-factor = 4.6%. [e] Experimental data are unavailable or are uncertain (see Methods). [f] Taken from CSD entry KIDREU01; R-factor = 2.64%. [g] Taken from CSD entry XUXLUX; R-factor = 2.79%. [h] Taken from CSD entry REMNAY; R-factor = 4.24%. [i] Taken from CSD entry VOGDUQ; R-factor = 4.6%.

Table 2. Comparison between Computed[a]and Experimental[b] Incremental Free Energies (in kcal/mol) at 298 K for $[Me(H_2O)_n{\cdot}(H_2O)_m]^{q+} + H_2O \rightarrow [Me(H_2O)_{n+1}{\cdot}(H_2O)_m]^{q+}$ or $[Me(H_2O)_n{\cdot}(H_2O)_{m+1}]^{q+}$

$n \rightarrow n+1$ or $n+m \rightarrow$ $n+(m+1)$	Li^+	Na^+	K^+	Rb^+
$0 \rightarrow 1$	−29.2	−18.7 (−17.6)	−12.4 (−11.4)	−9.5 (−9.6)
$1 \rightarrow 2$	−22.6 (−18.9)	−15.4 (−13.2)	−10.6 (−8.9)	−8.7 (−7.0)
$2 \rightarrow 3$	−14.0 (−13.3)	−10.0 (−9.3)	−6.7 (−6.3)	−5.9 (−5.0)
$3 \rightarrow 4$	−8.5 (−7.5)	−7.3 (−6.3)	−6.4 (−4.4)	−5.4 (−3.8)
$4 \rightarrow 5$	4.1	4.7	2.6	3.8
$4 \rightarrow 4+1$	−2.8 (−4.5)[c]	−2.1 (−3.9)[c]	−2.7 (−3.2)[c]	−1.5 (−2.8)[c]
$5 \rightarrow 6$	4.4	1.0	−0.3	−5.8
$5 \rightarrow 5+1$	[d]	−3.9	−0.6	−3.6
$4+1 \rightarrow 4+2$	−0.9 (−2.5)[c]	−2.4 (−2.9)[c]	−0.9 (−2.3)[c]	−0.9

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$5 \rightarrow 6$	−16.4 (−16.0)	−15.8 (−16.1)	−13.5 (−14.5)	−10.8 (−12.6)
$6 \rightarrow 7$	[d]	−7.7	−10.2 (−10.5)	−11.8 (−10.0)
$6 \rightarrow 6+1$	−10.1 (−12.8)[c]	−11.7 (−10.9)[c]		
$7 \rightarrow 8$		6.2	−1.3	+1.1
$7 \rightarrow 7+1$		−9.0 (−9.6)[c]	−10.5 (−9.3)[c]	−6.4 (−8.8)[c]
$6+1 \rightarrow 6+2$		−8.8 (−9.6)[c]		
$8 \rightarrow 9$			−3.3	−2.8
$8 \rightarrow 8+1$				−7.5 (−7.8)[c]
$7+1 \rightarrow 8+1$				−0.1
$7+1 \rightarrow 7+2$				−4.8 (−7.8)[c]
$7+1 \rightarrow 9$				+5.6

[a] Computed using eq 2 with the electronic energies E_{elec} evaluated at the B3-LYP/(6-311++G(2df,2dp)/SDD)//B3-LYP/(6-31G**/SDD) level and the vibrational frequencies scaled by an empirical factor of 0.9613 (see Methods). [b] Where available, experimental values from Kebarle and co-workers are given in parentheses.[28,29] [c] The experimental value matches the computed number for $[Me(H_2O)_n{\cdot}(H_2O)_m]^{+q} + H_2O \rightarrow [Me(H_2O)_n{\cdot}(H_2O)_{m+1}]^{+q}$ better than that for the corresponding $n \rightarrow n+1$ reaction. [d] A local minimum for the $[Me(H_2O)_n{\cdot}(H_2O)_{m+1}]^{+q}$ product could not be found.

and alkaline earth metal ions studied. Vibrational frequencies were computed using the same B3-LYP/6-31G** method. The fully optimized structures do not contain any imaginary modes, verifying that they are indeed potential energy minima.

Gas-Phase Free-Energy Calculations. The gas-phase free energy, ΔG^1, for eq 1 at room temperature, $T = 298$ K, was computed according to

$$\Delta G^1 = \Delta E_{elec} + \Delta E_T + \Delta PV - T\Delta S \qquad (2)$$

Table 3. Calculated Free Energies (in kcal/mol) for $Me^+ + n(H_2O) \rightarrow [Me(H_2O)_{n-m}{\cdot}(H_2O)_m]^+$

$n+m$	Li^+	Na^+	K^+	Rb^+
1	−29.2	−18.7	−12.4	−9.5
2	−51.7	−34.1	−23.0	−18.2
3	−65.8	−44.1	−29.7	−24.1
4	−74.3	−51.4	−36.0	−29.6
5	−70.2	−46.7	−33.5	−25.8
(4 + 1)[a]	−77.1	−53.5	−38.8	−31.1
6	−65.8	−45.8	−33.7	−31.6
(5 + 1)[a]	[b]	−50.7	−34.1	−29.3
(4 + 2)[a]	−78.0	−55.9	−39.6	−32.0

[a] The metal ion is bound to one or two water molecules in the second shell. [b] A local minimum for the $[Li(H_2O)_5{\cdot}(H_2O)_1]^+$ product could not be found.

Table 4. Comparison between the Metal CNs of Isolated Alkali Ion−Water Complexes from This Work with Those from Previous Studies in the Gas Phase, in Crystal Structures, and in Aqueous Solution

method	Li^+	Na^+	K^+	Rb^+
gas-phase calculations, this work	4	4	4	4 or 6
gas-phase calculations, previous studies	4[a]	4 or 5[b]	4, 5, or 6[c]	4 or 5[d]
gas-phase experiments and calculations	4[e]	4[e,f]	4[e]	4[e]
crystal structures of the hydrated metal	4[g](13)	4[g](2)	[h]	[h]
crystal structures of the hydrated metal	5[g](1)	6[g](3)		
solution experiments	4[i]	4 or 6[i]	4 or 6[i]	3.5[j]

[a] From refs 8 and 10. [b] From ref 4. [c] From ref 9. [d] From ref 12. [e] From Table 2, see text. [f] From ref 31. [g] From Table 5 in ref 1; the number in parentheses is the number of CSD structures with that CN. [h] No high-resolution (R-factor ≤ 5%) crystal structure of the ion bound only to water molecules is found in the current CSD. [i] From ref 29. [j] From ref 33.

where E_{elec} is the electronic energy, E_T is the thermal correction term including the zero-point energy, PV is the work term, and S is the entropy. The electronic energies E_{elec} were evaluated using the Gaussian 03 program[13] with the B3-LYP functional in conjunction with the SDD basis set for Rb^+, Sr^{2+}, and Ba^{2+} and the 6-311++G(2df,2dp)[21] basis set for all the other atoms. The latter basis set was chosen because it yields a water dipole moment of 1.94 D that is reasonably close to the experimental value (1.85 D) and could therefore reliably describe the charge−dipole interactions that dictate the metal−water interactions. The diffuse functions and extra polarization functions in the 6-311++G(2df,2dp) basis set are needed to also reliably describe the significant polarization effects in the ion−water interactions, which largely account for the nonadditive, many-body contributions to the binding energy.[6,22] The computed energies for eq 1 were corrected for basis-set superposition errors using the counterpoise method.[23] The thermal energy, E_T, and the total entropy, S, were evaluated using standard statistical mechanical formulas after scaling the vibrational frequencies by an empirical factor of 0.9613.[24] Partial atomic charges were also calculated using natural population analysis at the B3-LYP/(6-311++G(2df,2dp)/SDD)//B3-LYP/(6-31G**/SDD) level.[25]

CSD Structures. As we determine the preferred number of water molecules bound to a given metal ion in the gas phase, we compare this number to that observed in CSD structures of the respective metal ion bound to only water molecules. These CSD structures were obtained in previous work,[1] where the Cambridge Structural Database version 5.25[26] and ConQuest version 1.6[27] were used to search for structures with R-factor ≤ 0.05 for all group IA and IIA

---

(21) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(22) Dudev, T.; Lim, C. *J. Phys. Chem. A* **1999**, *103*, 8093.

(23) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(24) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(25) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

Table 5. Calculated Free Energies (in kcal/mol) for $Me^{2+} + n(H_2O) \rightarrow [Me(H_2O)_{n-m}{\cdot}(H_2O)_m]^{2+}$ [a]

$n + m$	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	−141.8	−76.5	−51.0	−41.3	−34.5
2	−251.6	−141.0	−93.3	−76.8	−62.5
3	−318.5	−188.9	−128.9	−105.4	−87.0
4	−357.4	−225.6	−157.2	−131.1	−109.1
5 (4+1)	−360.6 (−377.7)	−245.9	−177.2	−147.9	−124.5
6 [4+2]	−364.5 [−396.7]	−262.3	−193.0	−161.5	−135.3
7 (6+1)		(−272.2)[b]	−200.7 (−204.6)	−171.7	−147.1
8 (7+1) [6+2]			−199.7 (−209.7) [−213.4]	−173.0 (−182.2)	−146.0 (−153.5)
9 (8+1) [7+2]				−176.3	−148.8 (−153.5) [−158.3]

[a] Numbers in round parenthesis and square brackets correspond to structures with one or two water molecules, respectively, in the second shell. [b] Geometry optimization of the metal ion bound to all the water molecules in the first shell yielded an unstable structure that spontaneously decomposed to a lower CN structure with one water in the second shell.

metal ions bound to only water molecules. No such structures with R-factor ≤ 0.05 were found for K^+ and Rb^+ bound to only water molecules. The metal−aqua complex structures were analyzed for the metal CNs according to the atoms that were "connected" to a given metal ion in the PDB coordinate file. However, for the single Ba^{2+}−aqua complex structure (CSD entry, ICEKAD), the Ba^{2+} CN is 9 in the chemical formula and diagram but 12 in the 3D visualizer. Because of the ambiguity in the Ba^{2+} CN, the ICEKAD structure was not used in the analyses below.

3. Results

Comparison Between Computed and Experimental Geometries. For a metal−water complex of a given CN, comparison of the average metal−O(water) distance in the B3-LYP/(6-31G**/SDD) optimized structures with that in the respective CSD structure of the metal−aqua complex with the lowest R-factor shows that the average metal−O(water) distances in the optimized gas-phase structures are consistently greater than those in the CSD crystal structures by 0.02−0.09 Å (Table 1). The discrepancy between the experimental and computed metal−O(water) distances is partly due to the crystal structures being perturbed by the presence of counterions, as evidenced by the unequal bond distances observed for Be^{2+}, Mg^{2+}, and Sr^{2+}. For example, the fully optimized hexahydrated Mg^{2+} structure is fully symmetric with a Mg^{2+}−O distance of 2.10 Å, whereas the respective CSD structure, XUXLUX, is slightly distorted by a counterion, yielding unequal Mg^{2+}−O distances that differ by up to 0.04 Å (Table 1). It is also partly because the CSD structures are in the crystalline phase, as opposed to gas phase in the calculations, and were solved by X-ray diffraction, which gives atomic coordinates that are at the center of gravity of the electron density of the atom rather than nuclear positions. Considering these differences between the CSD and the computed structures, the B3-LYP/(6-31G**/SDD) method yields reasonably accurate geometries for group IA and IIA cations complexed with water molecules. Furthermore, previous work has shown that substantial deviation from experimental geometries has negligible influence on the metal−water interaction energy, e.g., when the error in the Ca^{2+}−O bond distance was reduced to 0.05 Å, the Ca^{2+}−water interaction energy changed by only 0.16 kcal/mol.[7]

Table 6. Comparison of the Metal CNs in Gas-Phase Alkali Earth Ion−Water Complexes from This Work with the Respective CNs from Previous Studies in the Gas Phase, in Crystal Structures, and in Aqueous Solution

method	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
gas-phase calculations, this work	4	6	6	7	7
gas-phase calculations, previous studies	4[a]	6[a]	[b]	[b]	[b]
gas-phase experiments and calculations	[b]	6[c]	6[c]	7[c]	7[c]
crystal structures of the hydrated metal	4[d] (3)	6[d] (65)	6[d] (2), 7[d] (5), 8[d] (1)	8[d] (1)	9[d] (1)
solution experiments	4[e]	6[e]	6, 7, or 8[e]	8[e]	9.5[e]

[a] From ref 5. [b] No data available. [c] From Table 2, see text. [d] From Table 5 in ref 1; number in parentheses is the number of CSD structures with that CN. [e] From ref 29.

Comparison Between Computed and Experimental Incremental Free Energies. To assess the accuracy of the free energies computed using eq 2 and the B3-LYP/(6-311++G(2df,2dp)/SDD) energies, we compared the $n \rightarrow n + 1$ free energies for the successive binding of water molecules to each alkali or alkaline earth ion−water complex, i.e., $H_2O + [Me(H_2O)_n{\cdot}(H_2O)_m]^{q+} \rightarrow [Me(H_2O)_{n+1}{\cdot}(H_2O)_m]^{q+}$, to the respective experimental numbers in the gas phase where available (see Table 2). Note that it is difficult to obtain reliable experimental $0 \rightarrow 1$ free energies for Li^+.[28,29] In addition, experimental incremental free energies for group IIA dications when $n < 5$ have not been measured, because these metal complexes possess very large bond energies; thus, they require very high temperatures to dissociate the metal−O(water) bond, which was inaccessible in the experimental studies.[28,29] The experimental error in the incremental free energies in Table 2 has been estimated to be ±1 kcal/mol. In cases where there is a clear mismatch between the computed and experimental $n \rightarrow n + 1$ gas-phase free energies, the $n + m \rightarrow n + (m + 1)$ free energy for binding of a water molecule in the second shell, i.e., $[Me(H_2O)_n{\cdot}(H_2O)_m]^{q+} + H_2O \rightarrow [Me(H_2O)_n{\cdot}(H_2O)_{m+1}]^{q+}$, was also computed. The notation $n + m$ denotes the number of water molecules in the first and second hydration shells, respectively.

The biggest errors in the computed free energies probably stem from the harmonic approximation for the lower vibrational modes; however, the errors in the reactant metal−

---

(26) Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380.
(27) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr, Sect. B.* **2002**, *58*, 389.
(28) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.
(29) Peschke, M.; Blades, A. T.; Kebarle, P. *J. Phys. Chem. A* **1998**, *102*, 9978.

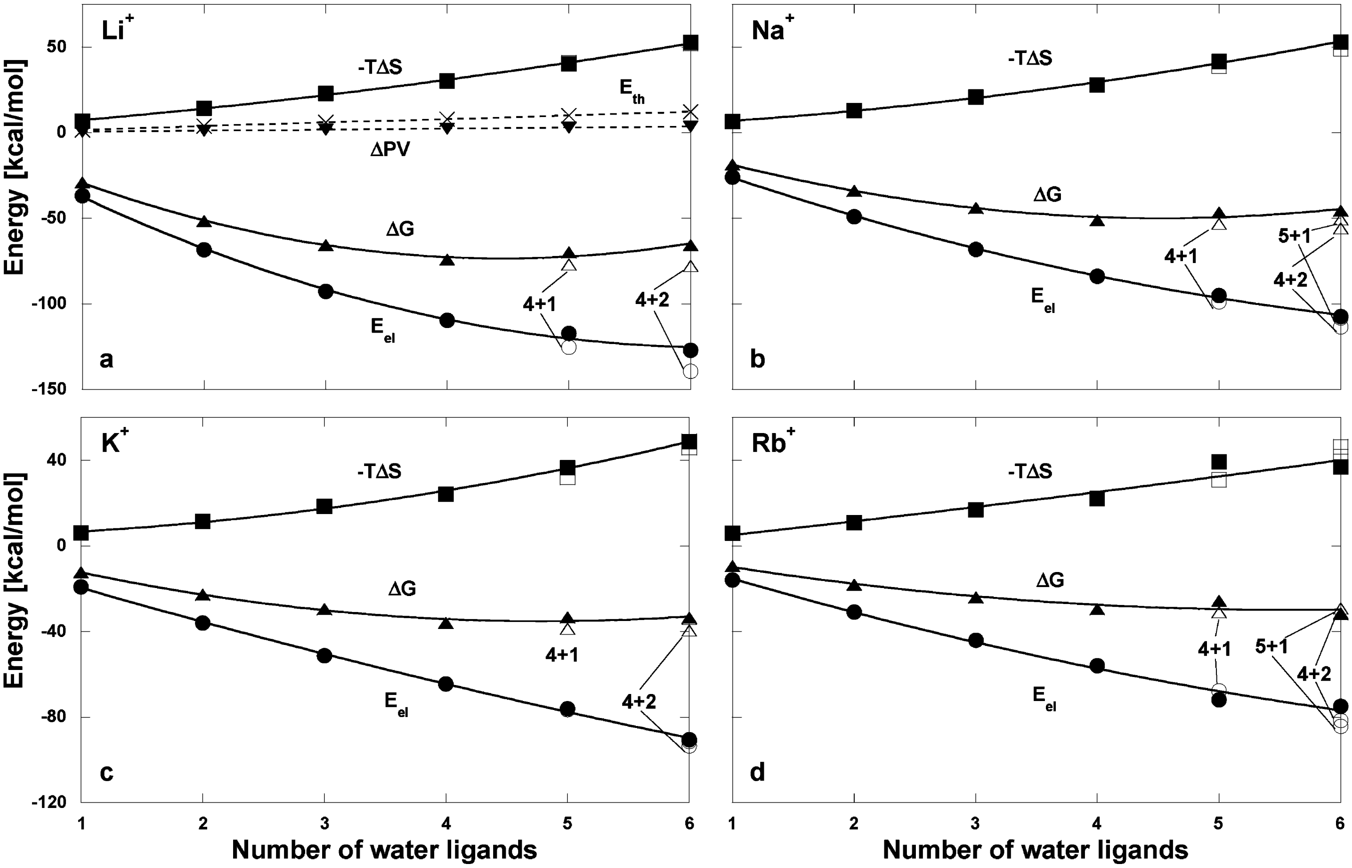

Figure 1. Calculated free-energy components (see eq 2) for (a) Li^+, (b), Na^+, (c) K^+, and (d) Rb^+ as a function of the number of water ligands. As the work and thermal correction terms in eq 2 are relatively small and insensitive to the CN, as shown in panel a, they are omitted for clarity in b−d. The filled symbols correspond to structures with all the water molecules bound directly to the metal ion, whereas the open symbols correspond to the respective structure with one or two water molecules in the second shell. Note that the 6 + 0 and 5 + 1 K^+ aqua complexes have nearly identical free energies (−34 kcal/mol), whereas the 6 + 0 and 4 + 2 Rb^+ aqua complexes have nearly identical free energies (−32 kcal/mol); thus, the corresponding open and filled symbols overlap.

aqua complex partly cancel those in the corresponding product metal complex with one more inner-shell water molecule, allowing for reasonable agreement between the experimental gas-phase incremental free energies and the computed $n \rightarrow n + 1$values. For group IA monocations, the experimental values match the computed $n + m \rightarrow n + (m + 1)$ free energies better than the corresponding computed $n \rightarrow n + 1$ numbers when $n \geq 4$. For example, the computed $4 \rightarrow 5$ incremental free energies are unfavorable (positive), whereas the computed $4 + 0 \rightarrow 4 + 1$ values are favorable (negative), in accord with the respective experimental numbers. These results suggest that when the alkali metal ion has become tetrahydrated in the gas phase, it prefers to bind indirectly to a fifth or sixth water molecule in the second shell rather than expand its CN to bind directly to additional water molecules. On the other hand, for group IIA dications, the experimental values match the computed $n + m \rightarrow n + (m + 1)$ free energies better than the corresponding computed $n \rightarrow n + 1$ numbers when $n \geq 6$ for Mg^{2+} and Ca^{2+} and when $n \geq 7$ for Sr^{2+} and Ba^{2+}.

In the following, we present first our findings on the preferred gas-phase CNs of isolated metal−aqua complexes and compare them with the respective numbers obtained in previous theoretical studies (Tables 3−6). We also compare the preferred gas-phase CN of an isolated metal−aqua complex with the respective available experimental number determined (i) in the gas phase, (ii) in crystal structures of the given metal ion bound to only water molecules, and (iii) in aqueous solution (Tables 4 and 6).

Gas-Phase CNs of Group IA Metal Hydrates. The preferred gas-phase CN for each alkali metal ion complexed with water molecules was determined by computing the gas-phase free energies for $Me^+ + n(H_2O) \rightarrow [Me(H_2O)_{n-m}\cdot(H_2O)_m]^+$ as a function of the number of water molecules, n (see Table 3). For each alkali metal ion, the calculated free energy for $Me^+ + n(H_2O) \rightarrow [Me(H_2O)_{n-m}\cdot(H_2O)_m]^+$ and its component binding energy (ΔE_{elec} in eq 2) and entropy term ($-T\Delta S$ in eq 2) are shown in Figure 1.

Lithium. Lithium differs from the other group IA cations in that it has no second-shell electrons. Yet its Pauling ionic radius, 0.74 Å,[30] is similar to that of Mg^{2+}, 0.72 Å;[30] hence, Li^+, like Mg^{2+}, can accommodate six water molecules in the first shell. Indeed, the binding energy (Figure 1a, filled circles) of hexa- (6 + 0) or penta- (5 + 0) hydrated Li^+ is more negative than that of the 4 + 0 tetrahydrate. In contrast to the binding energy, which becomes more favorable (more negative) with an increasing number of metal-bound water molecules, the corresponding entropy term (Figure 1a, filled squares) becomes more unfavorable with increasing CN. On the other hand, the work and thermal correction terms in eq

2 are relatively small and insensitive to the CN (Figure 1a, inverted triangles and crosses). Because of the opposite enthalpic and entropic effects, the gas-phase free energy is a minimum when the CN of Li^+ is 4 rather than 6 (Figure 1a, filled triangles, and Table 3). That Li^+ prefers a gas-phase CN of 4 is also supported by the more-favorable free energies found for the 4 + 1 (−77 kcal/mol) and 4 + 2 (−78 kcal/mol) structures with one and two second-shell water molecules, respectively, relative to those of the corresponding 5 + 0 (−70 kcal/mol) and 6 + 0 (−66 kcal/mol) structures (Table 3), in accord with previous electronic structure calculations.[8,10]

The preferred Li^+ CN of 4 found in the gas phase is consistent with that observed in the CSD structures of Li^+ bound to only water molecules: 13 structures show a tetrahydrated Li^+, whereas only one shows a pentahydrated Li^+.[1] Interestingly, bulk solvent effects do not seem to affect the preferred Li^+ CN, which is also found to be 4 in aqueous solution from X-ray diffraction data[31] as well as from QM/MM[8] and ab initio MD simulations.[10,11] Thus, Li^+ prefers a CN of 4 in the gas phase, in the crystalline state, and in aqueous solution (Table 4).

Sodium and Potassium. As for Li^+, the binding energies of Na^+ and K^+ aqua complexes become more favorable with increasing CN so that the hexa- or pentahydrated metal ion is energetically more stable than the tetrahydrated one (Figure 1b,c, filled circles). However, the magnitude of the entropy term, $|T\Delta S|$, is comparable to that of the electronic energy, and the entropic penalty for adding one or two water molecules to the tetrahydrated metal ion exceeds the respective energy gain. Hence, for Na^+ and K^+, the binding gas-phase free energy as a function of the number of water ligands is a minimum when the CN is 4 (Figure 1b,c). Furthermore, the gas-phase free energies of penta (5 + 0) and hexa (6 + 0) hydrated Na^+ and K^+ are less favorable than those of the respective 4 + 1 and 4 + 2 structures (Table 3), in accord with previous ab initio calculations of Na^+[32] and K^+ aqua complexes.[9] In contrast to the preferred gas-phase CN of 4 for Na^+ and K^+ predicted from the present B3-LYP/(6-311++G(2df,2pd)/SDD)//B3-LYP/(6-31G**/SDD) calculations, MP2/TZ2P//HF/TZ2P binding free-energy calculations predict equally probable CNs of 4 and 5 for penta- and hexa-aqua Na^+ complexes[4] and CNs of 4, 5, and 6 for hexa-aqua K^+ complexes[9] at 298 K and 1 atm.

Although previous MP2 calculations[4,9] predict no single preferred gas-phase CN for Na^+ and K^+ bound to water molecules, infrared photodissociation spectra of hydrated Na^+ clusters show a tetrahedral first hydration shell of Na^+ in the gas phase,[33] in accord with our DFT calculations. On the other hand, high-resolution (R-factors ≤ 0.05) crystal structures of hydrated Na^+ in the CSD have inconclusive CNs; the Na^+ CN is 4 in two CSD structures (GIXBAQ and WABPIZ), but 6 in three CSD structures (QUQKES, FASCEI, and XUKWOP). A reliable CN for K^+ is difficult to obtain from crystal structures of hydrated K^+. As the K^+−O(water) distance (2.7 Å) is comparable to the O(water)−O(water) distance (2.8 Å)[34] and a water molecule can hydrogen bond to four ligands, it would be difficult to differentiate between K^+ and O when K^+ is bound to four ligands. Furthermore, the residence time for a water oxygen atom to stay in the first shell of K^+ is very short ($<1 \times 10^{-10}$ s),[31] making the crystallization process sensitive to fluctuations. In aqueous solution, both CNs 4 and 6 are found for Na^+ and K^+ from X-ray diffraction data.[31] A CN in aqueous solution that is larger than that in the gas-phase aqua complex can be attributed to the weaker ion−O(water) interactions in the larger hydrated metal ion being compensated by an energy gain from additional hydrogen-bonding interactions between first- and second-shell water molecules.[4]

Rubidium. For the largest nonradioactive group IA metal ion considered here, the preferred gas-phase CN is not solely imposed by the entropic cost of localizing the metal-bound water molecules, as it is for the smaller alkali metal ions. Similarly to Li^+, Na^+, and K^+, the Rb^+ binding energy becomes more favorable with increasing CN (Figure 1d), as the large Rb^+ ion can easily accommodate many water molecules in the first shell. In contrast to Li^+, Na^+, and K^+, the free energy of hexahydrated Rb^+ (−31.6 kcal/mol) is slightly more favorable than that of the tetrahydrated metal cation (−29.6 kcal/mol), indicating that the entropic cost of immobilizing water molecules does not outweigh the energy gain in the Rb^+−water interactions. However, it is similar to the free energy of the isomeric 4 + 2 structure (−32.0 kcal/mol, Table 3). The latter is energetically more stable than the respective structure with all six water molecules in the first shell (Figure 1d) because of the stronger hydrogen-bonding interactions between first-shell and second-shell water molecules, as compared to the relatively weak electrostatic interactions between the large Rb^+ and first-shell water molecules. Previous DFT calculations also support the present finding that Rb^+ does not exhibit a strong preference for a specific CN; however, they predict equally probable gas-phase CNs of 4 and 5 (rather than 4 and 6 found herein) for Rb^+.[12]

Because the free energy difference between the 6 + 0 and 4 + 2 structures differs by less than 1 kcal/mol, the observed gas-phase CN would be expected to be sensitive to the experimental conditions such as the presence of counterions and pH. No high-resolution crystal structure of Rb^+ complexed with water molecules is currently available in the CSD, although an NMR measurement reported a CN of 3.5 for Rb^+ in aqueous solution.[35]

Gas-Phase CNs of Group IIA Metal Hydrates. The preferred gas-phase CN for each alkaline earth metal ion complexed with water molecules was determined by com-

---

(30) Marcus, Y. *Chem. Rev.* **1988**, *88*, 1475.
(31) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.
(32) Lybrand, T. P.; Ghosh, I.; McCammon, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 7793.
(33) Patwari, N. G.; Lisy, J. M. *J. Chem. Phys.* **2003**, *118*, 8555.
(34) Richens, D. T. *The Chemistry of Aqua Ions*; John Wiley & Sons: New York, 1997.
(35) Vorgin, J.; Knapp, P. S.; Flint, W. L.; Anton, A.; Highberger, G.; Malinowski, E. R. *J. Chem. Phys.* **1971**, *54*, 178.

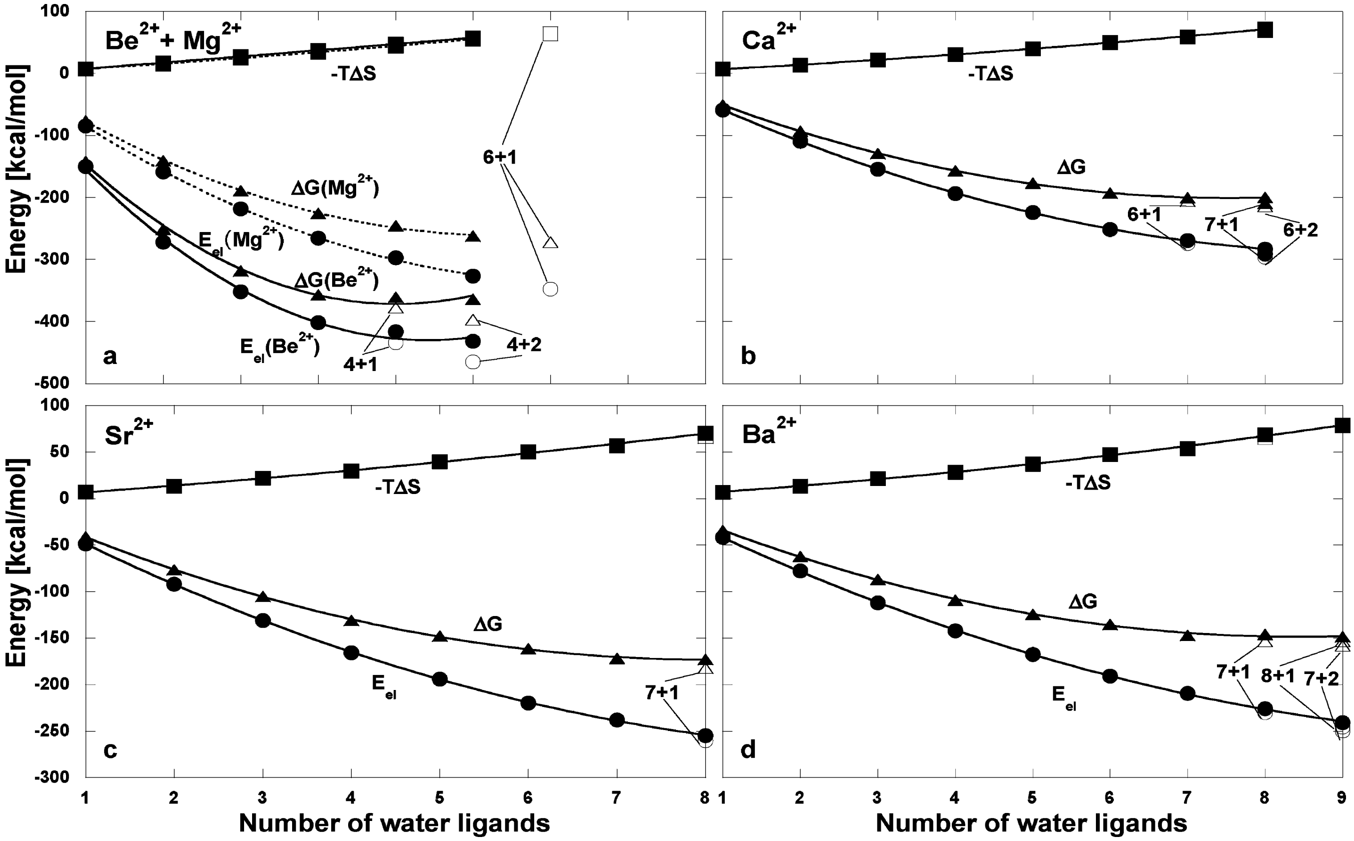

Figure 2. Calculated free-energy components (see eq 2) for (a) $Be^{2+}$and Mg^{2+}, (b) Ca^{2+}, (c) Sr^{2+}, and (d) Ba^{2+} as a function of the number of water ligands. The filled symbols correspond to structures with all the water molecules bound directly to the metal ion, whereas the open symbols correspond to the respective structure with one or two water molecules in the second shell.

puting the gas-phase free energies for $Me^{2+} + n(H_2O) \rightarrow [Me(H_2O)_{n-m}\cdot(H_2O)_m]^{2+}$ as a function of n (see Table 5).

Beryllium. As for Rb^+, both the binding energy and free energy become more favorable as more water molecules become bound to Be^{2+} (Figure 2a) so that penta- or hexahydrated Be^{2+} is apparently more stable than the tetrahydrated metal ion (Table 5). However, the structure with four water molecules in the first shell and one or two water molecules in the second shell has a much more favorable free energy than the five- or six-coordinated structure by ~17 and ~32 kcal/mol, respectively (Figure 2a and Table 5). The preference for a gas-phase CN of 4 appears to be an effect of the hybrid sp^3 orbitals formed, which disfavor bonding to more than four water molecules.

The predicted gas-phase CN of 4 for Be^{2+} is in accord with previous MP2/6-311++G**//RHF/6-31G* free-energy calculations.[5] A CN of 4 is also found in the tetrahydrated Be^{2+} structures in the CSD (KIDREU, KIDREU01, MINKUP) and in aqueous solution, as determined by X-ray diffraction and NMR.[31] That tetrahydrated Be^{2+} is a distinct stable structural entity in aqueous solution is consistent with the relatively long residence time ($\geq 3 \times 10^{-4}$ s)[31] of its first-shell water oxygen atoms from NMR studies at 25 °C.[36] Thus, as with Li^+, Be^{2+} prefers a CN of 4 in the gas phase, in the crystalline state, and in aqueous solution.

Magnesium. No structure with seven water molecules in the first shell could be found for Mg^{2+}, as one of the water molecules spontaneously transferred to the second shell during geometry optimization. Hence, Figure 2a shows the thermodynamic parameters for complexes with up to six first-shell water ligands only. As for Be^{2+}, both the binding energy and free energy become more favorable with increasing CN (Figure 2a, dotted curves). The octahedrally hydrated Mg^{2+} is stable relative to other hydration geometries/numbers in the gas phase as its free energy is much more favorable than the free energy of the next most stable structure, $[Mg(H_2O)_5]^{2+}$, by ~16 kcal/mol (Table 5).

The strong preference for Mg^{2+} to be hexahydrated in the gas phase is in accord with previous MP2/6-311++G**//RHF/6-31G* free-energy calculations.[5] A CN of 6 is also observed in 65 CSD aqua complexes[1] and in aqueous solution.[31] As with that of Be^{2+}, the residence time of water oxygen atoms in the first-shell of Mg^{2+} is relatively long (~1×10^{-5} s),[31] indicating a stable hexahydrated Mg^{2+} complex in aqueous solution.[36] Thus, similar to Li^+ and Be^{2+}, the preferred CN of Mg^{2+} appears to be independent of its phase.

Calcium. Although the binding energy becomes more favorable with increasing CN (Figure 2b), the free energy of heptahydrated (7 + 0) Ca^{2+} is slightly more favorable than that of octahydrated (8 + 0) Ca^{2+} (by 1 kcal/mol) but less favorable than that of the isomeric 6 + 1 structure (by 4 kcal/mol, Table 5). That Ca^{2+} prefers a gas-phase CN of 6 rather than 7 is also supported by the more favorable free

---

(36) Burgess, M. A. *Metal Ions in Solution*; Ellis Horwood: Chichester, U.K., 1978.

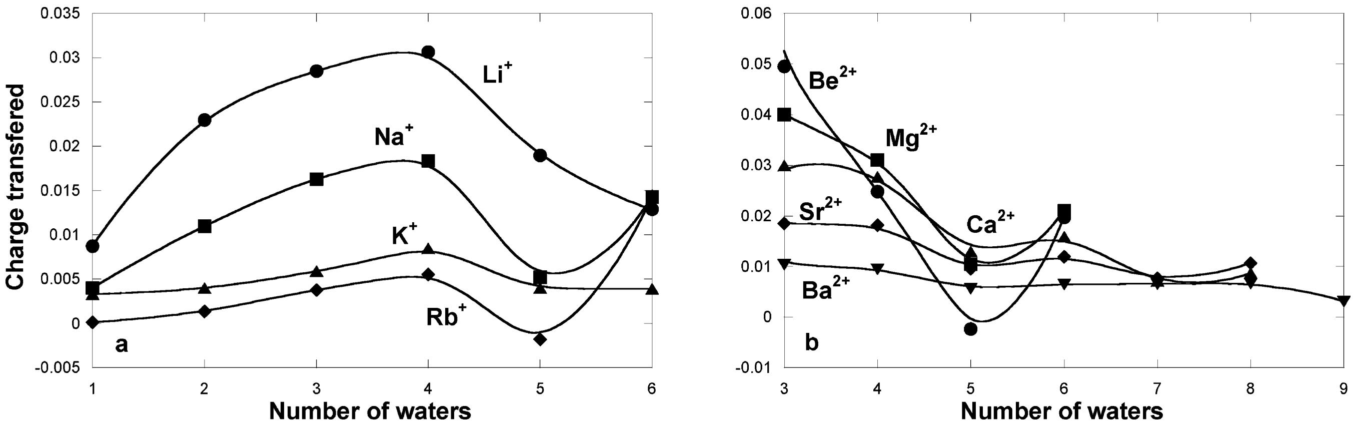

Figure 3. Calculated incremental charge transfer vs number of metal-bound water molecules for (a) alkali metal ions and (b) alkaline earth metal ions, where the charges are derived from a natural population analysis at the B3-LYP/(6-311++G(2df,2pd)/SDD)//B3-LYP/(6-31G**/SDD) level.

energy of the 6 + 2 structure (−213 kcal/mol), as compared to that of the corresponding 7 + 1 structure (−210 kcal/mol, Table 5). It is also supported by the experimental incremental gas-phase free energies in Table 2. The measured 6 → 7 gas-phase free energy (−10.9 kcal/mol) is closer to the computed 6 → 6 + 1 free energy (−11.7 kcal/mol) than to the computed 6 → 7 number (−7.7 kcal/mol). However, unlike Be^{2+} and Mg^{2+}, Ca^{2+} does not exhibit a strong preference for a specific CN, as the 6 + 1 and 6 + 2 structures are only ~4 kcal/mol more stable than the corresponding 7 + 0 and 7 + 1 structures, respectively (Table 5).

The relatively small free-energy difference between Ca^{2+} aqua complexes containing six and seven water molecules in the first shell suggests that both CNs may be observed, depending on the experimental conditions. Indeed, both CNs are observed in the CSD structures of Ca^{2+} aqua complexes, where two (NOGLEA, BIHNIQ) are 6 + 1 hydrated, three (REMNAY, RUMQOF, WIKXET) are 7 + 0 hydrated, and two (HEPHOZ, ZZZKVU10) are 7 + 1 hydrated.[1] In analogy to K^+, the residence time for the Ca^{2+}-bound water oxygen is also very short ($<1 \times 10^{-10}$ s),[31] further implying a variable CN for Ca^{2+}. Thus, CNs of 6, 7, and 8 have been reported for Ca^{2+} in aqueous solution.[31,37] Recent X-ray diffraction data, however, indicate a CN of 8 for a 1 M $CaCl_2$ solution, with the CN decreasing as the $CaCl_2$ salt concentration increases.[37] This suggests that the Ca^{2+} CN is 8 when the second shell is fully hydrated and hydrogen-bonding interactions between first- and second-shell water molecules are maximized but is less than 8 when the second shell is only partially hydrated, in accord with the results in Table 5 (see above).

Strontium and Barium. The binding energy becomes more favorable as the number of metal-bound water molecules increases up to 8 for Sr^{2+} and 9 for Ba^{2+} (Figure 2c,d). No stable structures could be found for nonahydrated Sr^{2+} and decahydrated Ba^{2+}, as one of the water molecules spontaneously transferred to the second shell during geometry optimization. Sr^{2+} prefers a gas-phase CN of 7 rather than 8, as the free energy of 8 + 0 octahydrated Sr^{2+} is ~9 kcal/mol less favorable than that of the 7 + 1 structure (Table 5). Likewise, Ba^{2+} also prefers a gas-phase CN of 7 rather than 8; The free energy of the 7 + 1 structure is more favorable than that of the 8 + 0 isomer (by 7.5 kcal/mol), whereas the free energy of the 7 + 2 structure is more favorable than that of the 8 + 1 or 9 + 0 structure by ~5 and 10 kcal/mol, respectively (see Table 5).

The predicted gas-phase CN of 7 for Sr^{2+} and Ba^{2+} is consistent with the finding that the measured 7 → 8 gas-phase free energies are much closer to the computed 7 → 7 + 1 free energy than to the computed 7 → 8 value (see Table 2). However, it is smaller than the CN of 8 found in the single high-resolution crystal structure of a Sr^{2+} aqua complex (VOGDUQ). In aqueous solution, X-ray diffraction data[31] indicate a CN of 8 for Sr^{2+} and 9.5 for Ba^{2+}, suggesting an expansion of the CN upon solvation.

Correlation Between the Preferred Gas-Phase CN and the Amount of Ligand → Metal Charge Transfer. The preferred gas-phase CN for the alkali cations appears to be correlated with the degree of charge transfer from the water molecules to the monocation, as shown in Figure 3a, which plots the incremental charge transferred to the metal ion upon addition of a water molecule; e.g., when the number of water molecules is five, Figure 3 gives the charge transferred to the metal ion when a water molecule binds to the tetrahydrated complex to form a pentahydrated one. For the alkali metal ions, the ligand → metal charge transfer reaches a maximum when forming the most preferred structure with a gas-phase CN of 4, followed by a steep decline for the pentahydrated structure. This behavior is not apparent for the alkaline earth metal ions (Figure 3b). For Be^{2+}, when its preferred gas-phase CN of 4 (see Table 5) is exceeded, it appears to exhibit back-transfer of charge from the metal to the ligand.

4. Discussion

Comparison with Previous Theoretical and Experimental Gas-Phase Studies. The present DFT calculations predict a CN of 4 for Li^+, Na^+, K^+, and Be^{2+}; 4 or 6 for Rb^+; 6 for Mg^{2+} and Ca^{2+}; and 7 for Sr^{2+} and Ba^{2+}, when these ions are bound to water molecules in the gas phase. Previous calculations on specific alkali or alkaline earth

---

(37) Megyes, T.; Grosz, T.; Radnai, T.; Bako, I.; Palinkas, G. *J. Phys. Chem. A* **2004**, *108*, 7261.

hydrates support the preferred gas-phase CNs found herein for Li^+, Na^+, K^+ Rb^+, Be^{2+}, and Mg^{2+} hydrates, but they predict an equally probable gas-phase CN of 5 for Na^+, K^+, and Rb^+ hydrates (see Table 4). The latter would be inconsistent with the experimental incremental gas-phase free energies. The computed free energy for binding a fifth water molecule directly to a tetrahydrated alkali ion in the gas phase is positive, in contrast to the respective experimental number, which is negative (see Table 2). Furthermore, infrared photodissociation spectra of hydrated Na^+ clusters show four rather than five water molecules bound directly to Na^+ in the gas phase.[33] The preferred gas-phase CNs for the alkali or alkaline earth hydrates found from matching the measured incremental gas-phase free energies with the respective computed values in Table 2 also support those found from the minimum in the gas-phase free energy of reaction 1 as a function of the number of water ligands in Tables 3 and 5.

Factors Governing the Gas-Phase CNs of Group IA Metal Hydrates. The present calculations also reveal the physical basis for the unexpected insensitivity of the CN on the size of the alkali metal ion. Although the monovalent alkali metal ions have larger ionic radii than the divalent alkaline earth metal ions and could accommodate more ligands, they have a smaller number of metal-bound water molecules in the gas phase than their divalent counterparts (see above). This is not solely because they have one less positive charge than the dications and therefore cannot bind a similar number of water molecules in the gas phase, because stable bound states with a CN larger than the preferred one can exist; for each alkali metal ion, the isolated hexa (6 + 0) or penta (5 + 0) aqua complex is energetically more stable than the tetra (4 + 0) one (Figure 1b−d). Rather, the monopositive charge on the group IA metal ions yields a net binding energy of magnitude comparable to the absolute entropy term, $|T\Delta S|$, at room temperature. Increasing the CN increases attractive electrostatic ion−water interactions, resulting in a more favorable binding energy; however, the water dipoles around the monocation become immobilized, increasing the entropic penalty, which thus prohibits a gas-phase CN greater than 4. In addition to the entropic effects, hydrogen-bonding interactions between first-shell and second-shell water molecules in the case of Rb^+ also enable the 4 + 2 structure to be competitive with the 6 + 0 isomer.

Factors Governing the Gas-Phase CNs of Group IIA Metal Hydrates. In contrast to group IA alkali ions, the calculations show an increase in the gas-phase CN of group IIA alkaline earth ions with increasing metal size (see Table 5). The dipositive charge on group IIA dications yields a net binding energy that is an order of magnitude greater than the binding energy of group IA monocations (compare Figures 1 and 2). On the other hand, the increased positive charge on group IIA dications does not significantly increase the entropic penalty, as $|T\Delta S|$ for group IA and group IIA metal ions are of similar magnitude. Consequently, the binding free energy is dictated by the binding energy, as shown in Figure 2a−d. In addition to the interactions between the metal dication and first-shell water molecules, hydrogen-bonding interactions between first-shell and second-shell water molecules appear to play a role in governing the first-shell CN.

Potential Factors for the Observed CN Change of Certain Metal Ions in Water. The present and previous results[4,37] provide clues to the factors affecting the change in the CN of a given metal−aqua complex upon solvation. In a concentrated solution where insufficient water molecules are available to form a complete second hydration shell, interactions between the metal ion and the first-shell water molecules are predominant; thus, the observed CN in solution is expected to be similar to the preferred CN of the respective metal−aqua complex with a few outer-shell water molecules. On the other hand, in a dilute solution where sufficient water molecules are available to form a complete second hydration shell, interactions between the first-shell and second-shell water molecules are maximized; thus, the observed CN of a given alkali/alkaline earth metal ion may be greater than the preferred CN found for the respective isolated metal hydrate if relative to the latter, the weaker metal−O(water) interactions in the aqua complex with a higher CN can be outweighed by an energy gain from additional hydrogen-bonding interactions between first- and second-shell water molecules in the larger aqua complex. Hence, the observed CN in aqueous solution may differ from that in the gas phase depending on (1) the number of water molecules available to form the second hydration shell, and (2) the balance between the net ion−O(water) interactions and the net first-shell−second-shell hydrogen-bonding interactions.

Acknowledgment. We thank Drs. C. S. Babu and T. Dudev for helpful discussions. This work was supported by the National Science Council, Taiwan (NSC Contract 91-2311-B-001) and the Institute of Biomedical Sciences, Academia Sinica.

Supporting Information Available: B3-LYP/6-311++G(2df,2pd) and B3-LYP/6-311++G(3df,3pd) electronic energies of $[Mg(H_2O)_6]^{2+}$ corresponding to different geometries (Table S1), Gaussian03 archives of the geometries and energies of group IA and IIA metal hydrates (Tables S2 and S3), and complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0519741