Comprehensive Study on the Solvation of Mono- and Divalent Metal Cations: Li^+, Na^+, K^+, Be^{2+}, Mg^{2+} and Ca^{2+}[†]

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Hydration of mono- and divalent metal ions (Li^+, Na^+, K^+, Be^{2+}, Mg^{2+} and Ca^{2+}) has been studied using the DFT (B3LYP), second-order Møller–Plesset (MP2) and CCSD(T) perturbation theory as well as the G3 quantum chemical methods. Double-ζ and triple-ζ basis sets containing both (multiple) polarization and diffuse functions were applied. Total and sequential binding energies are evaluated for all metal–water clusters containing 1–6 water molecules. Total binding energies predicted at lower levels of theory are compared with those from the high level G3 calculations, whereas the sequential binding energies are compared with available experimental values. An increase in the quality of the basis set from double-ζ to triple-ζ has a significant effect on the sequential binding energies, irrespective of the geometries used. Within the same group (I or II), the sequential binding energy predictions at the MP2 and B3LYP vary appreciably. We noticed that, for each addition of a water molecule, the change of the M-O distance in metal–water clusters is higher at the B3LYP than at the MP2 level. The charge of the metal ion decreases monotonically as the number of water molecules increase in the complex.

Introduction

The importance of metal ions and their diverse occurrences in chemistry and biochemistry are indubitable. In many biochemical systems, metal ions are of paramount importance.[1−4] Solvation of metal ions can lead to an understanding of the structures and functions of many biomolecules where metal ions play a role. Therefore, there is a substantial interest in their hydration characteristics.[5−18] Both mono- and divalent metal ions are well-known to be essential for the folding and stability of large RNA molecules that form complex and compact structures.[1,2] The study of hydrated metal ions in the gas phase provides a connection between the essential chemistry of the isolated ion and that in the solvent. Solvated ions also appear in high concentrations in living organisms, where their presence or absence can fundamentally alter the functions of life.[5] In fact, the structure and dynamics of solvation shells have a large impact on any chemical reaction of metal ions in solution.

Water solvation of alkali and alkaline earth metal ions has been extensively studied by different experimental techniques such as high-pressure mass spectrometry (HPMS), collision-induced dissociation (CID) using guided ion beam mass spectrometry, blackbody infrared radiative dissociation (BIRD) kinetics, and electrospray ionization (ESI) with Fourier transform mass spectrometry.[9−15] Experimental investigations have focused on the structures and energetics of solvated ions in the gas phase. In the past three decades, both X-ray and neutron diffraction techniques have been utilized to probe hydration numbers of the three alkali metal ions, Li^+, Na^+ and K^+.[7,8] Ambiguities still exist for the structures of these hydrated alkali metal ions.[8] William and co-workers have reported experimental evidence of two distinct gas phase structures of the hexahydrated Mg^{2+} ion. However, the exact nature of those two isomers could not be established by experiments.[13]

Solvation of alkali and alkaline earth metal ions has stimulated considerable theoretical interest.[15−28] Computational chemistry provides information on the arrangements of solvent molecules around metal ions, their binding energy, and the vibrational frequencies of the complexes that are often useful for experimentalists. Interplay between theory and experiment is crucial to obtain a molecular level understanding of ion solvation,[9−15] which will aid to attain correct mechanistic conclusions about biological control of ion movements. A combined experimental and theoretical investigation on the solvation of Ca^{2+} with water molecules has been carried out by Armentrout and co-workers. This study demonstrated how the sequential binding energies are changed by the addition of each water molecule.[15] Kim and co-workers have recently reported the predominance of electrostatic energies on the binding of alkali metal cations with water molecules. Further, they highlighted that the sum of induction and dispersion energies are almost canceled out by exchange-repulsion energy.[16] Merrill et al. have evaluated the performance of effective fragment potential method (EFP) with 6-31+G(d) basis set to the description of solvation in simple metal cationic systems.[17] Dipole moment and polarizabilities of $M(H_2O)_{1-8}$ ($M = Be^{2+}, Mg^{2+}, Ca^{2+}$, and Zn^{2+}) clusters were studied by Pavlov et al. using density functional theory,[18] and the study concluded that the energetic boundary between the first and the second solvation shell varies in size between the metal ions.

Glendening et al. have reported the binding energies of alkali and alkaline earth metal ions with water molecules using the Hartree–Fock (HF) and the second-order Møller–Plesset perturbation (MP2) methods.[22,23] According to their analysis,

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the HF method provides a reasonable description of cation−water interactions for small ($n = 1-3$) clusters, whereas it is not adequate for large clusters involving water−water hydrogen bonding. They also have revealed that $M(H_2O)_n$ [M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Ra^{2+}] clusters favor structures in which all water molecules directly coordinate to the dication in highly symmetric arrangements. Furthermore, they highlighted the importance of polarization contributions in the binding energies of $M(H_2O)_n$ clusters.[23] Sastry and co-workers studied the strength of metal ion interactions with the aromatic molecules. They reported that B3LYP and MP2 methods with a triple-ζ basis set containing a set of polarization and diffuse functions for both heavy atoms and hydrogens are necessary to model weak cation−aromatic molecule interactions.[24,25] The solvation and the size of the π-accepting group have a profound influence on the binding of metal ion with the aromatic systems.[26,27] Although these studies indicate good performance of metal ion interaction with organic and solvent molecules, it is advisable to apply the better functionals and refrain from using the current functional, such as B3LYP, in the future.[28]

Markham et al. reported that the $Mg^{2+}(H_2O)_5$ and $Mg^{2+}(H_2O)_6$ complexes with all water molecules in the first coordination shell are lower in energy than structures with one or two of the water molecules placed in the second coordination shell, when the same basis set is used for the calculations.[29] These observations are in excellent agreement with those of $Ca^{2+}(H_2O)_5$ and $Ca^{2+}(H_2O)_6$ complexes reported by Armentrout and co-workers.[15] In a study by Hashimoto et al., neutral and cationic $Li(H_2O)_n$ ($n = 1-6$ and 8) compounds were analyzed using ab initio methods and it was concluded that the first-shell hydration structure of the neutral Li atom is similar to that of Li^+ with the same $n \geq 4$.[30] An ab initio investigation of a full second solvation sphere of Li^+ ion ($[Li(H_2O)_4{}^+](H_2O)_n$, $n = 4$, 8) with a range of small and medium sized basis sets (STO-3G, 3-21G, 6-31G(d) and 6-31+G(d)) showed that a full second solvation sphere can significantly modify the vibrational spectra of aqueous metal ions.[31]

The importance of entropic contributions to the hydration of Mg^{2+} has been highlighted using ab initio and DFT methods.[32,33] A mass spectral analysis of alkali metal ion containing water clusters was performed by Steel et al. who observed the magic-number cluster of $M^+(H_2O)_{20}$ for Li, K, Rb and Cs cations.[34] Steel et al. also performed molecular dynamics (MD) simulations that suggested that a pentagonal dodecahedral network of water molecules surrounding a central ion is the stablest structure for $M^+(H_2O)_{20}$. Apart from this work, we have also come across several molecular dynamics simulations on the solvation of alkali, alkaline earth and first row transition metal cations.[35−39] Rode and co-workers performed molecular dynamics simulations to describe the nonadditive contributions in the first hydration shell of Na^+, K^+ and Mg^{2+} based on an ab initio QM/MM approach.[39] Spangberg et al. studied MD simulation on rate and mechanisms for water exchange around Li.[36]

In the present study, water molecules are added to metal ions [M = Li^+, Na^+, K^+, Be^{2+}, Mg^{2+} and Ca^{2+}] and the conformational space of these hydrated metal ion complexes [$M(H_2O)_n$; $n = 1-6$] is explored using ab initio and density functional theory methods with a range of basis sets. This benchmark study not only provides insight into the nature of solvation of metal ions but also establishes the method and basis set dependency of this solvation. Because the hydration of metal ions is a topic of great interest, it is necessary to identify theoretical methods that can satisfactorily reproduce experimental results at the lowest computational cost. Recently, Rao and Sastry have evaluated the importance of the method and the basis set for the accurate prediction of proton affinities of five-membered heterocyclic amines. It was concluded that the B3LYP functional performs slightly better than the wave function based methods like MP2.[40] In recent years, density functional theory, especially the B3LYP functional emerged as a method of choice compared to MP2, due to its computational economy. Thus, wherever possible, it has become a practice to employ this economical method instead of MP2 and CCSD(T). Therefore, the main objective of this paper is to assess the performance of the B3LYP (DFT), in comparison to the wave function based methods. We have taken the experimental sequential binding energies of hydration of Li^+, Na^+, and K^+ as reference values to evaluate the computational procedures.[9,10a,14] We do not have the experimental results of sequential binding energies for all of the hydrated complexes involving divalent ions; therefore, we have used high level G3 energies as reference values to assess various levels employed in this study.

Computational Methods

Initially, all metal−water complexes considered in the present study [$M(H_2O)_n$; $n = 1-6$] were explored by the B3LYP/6-31G(d) level to locate the minimum energy conformations on their respective potential energy surfaces. Vibrational frequency calculations were performed at the same level to ascertain the nature of the stationary points. Among the various possible conformers, the lowest energy structures were considered for further geometry optimizations at the B3LYP/6-31+G(d), B3LYP/6-311++G(d,p), MP2(FULL)/6-31+G(d), and MP2(FULL)/6-311++G(d,p) levels. Besides this, single point calculations were performed at the B3LYP/6-311++G(2d,2p), B3LYP/6-311++G(3d,3p), MP2(FULL)/6-311++G(2d,2p), MP2(FULL)/6-311++G(3d,3p), CCSD(T)/6-31+G(d) and CCSD(T)/6-311++G(d,p) levels using the geometries optimized at the B3LYP/6-311++G(d,p) and MP2(FULL)/6-311++G(d,p) levels.

Calculations were also performed by the Gaussian-3 (G3) method,[41] a composite technique that employs a sequence of ab initio molecular orbital calculations to estimate the total energy of a given molecular system at a level where it cannot be calculated directly. The GTlarge basis set, which is required in some of these calculations, is not available in Gaussian 03 for Ca and K. The GTlarge basis functions for Ca and K were taken from the study of Curtiss et al.,[42] and all the steps involved in the G3 calculation were done individually to obtain the G3 energy for the complexes containing K^+ and Ca^{2+} ions. To calculate the basis set superposition error (BSSE), we have used the counterpoise correction of Boys and Bernardi.[43] BSSE values obtained at the MP2(FULL)/6-31+G(d) and MP2(FULL)6-311++G(d,p) levels are used for BSSE corrections at the CCSD(T)/6-31+G(d) and CCSD(T)/6-311++G(d,p) levels, respectively. The B3LYP (DFT) and the MP2 wave function methods with 6-311++G(d,p) basis set were used to obtain the NPA charges. A method of “natural population analysis” (NPA) has been developed to calculate atomic charges and orbital populations of molecular wave functions in general atomic orbital basis sets. The natural population analysis is an alternative to conventional Mulliken population analysis, and seems to exhibit improved numerical stability and to better describe the electron distribution in compounds of high ionic character, for example, those containing metal atoms. In this study, we have used NPA to examine the charge transfer from water(s) to metal ion. All calculations were performed using Gaussian 03 program.[44]

Total and sequential binding energies were calculated using the following equations.

$$\mathrm{M} + n\mathrm{H_2O} \xrightarrow{\Delta E_{\mathrm{bind}}} \mathrm{M(H_2O)}_n$$

$$\mathrm{M} = \mathrm{Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}\text{and } Ca^{2+}};\ n = 1-6 \quad (1)$$

$$\mathrm{M(H_2O)}_n + \mathrm{H_2O} \xrightarrow{\Delta E_{\mathrm{seq}}} \mathrm{M(H_2O)}_{n+1}$$

$$\mathrm{M} = \mathrm{Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}\text{and } Ca^{2+}};\ n = 1-5 \quad (2)$$

Results and Discussion

The results of current work are arranged in the following order: First, we concentrate on the details of all conformations of metal−water clusters obtained by the B3LYP/6-31G(d) method. Second, we focus on the variation of M-O distances and hydrogen bond lengths between the B3LYP and MP2 methods with different basis sets. Third, the performance of methods and basis sets in the evaluation of total and sequential binding energies is presented. Finally, we turn to NPA charge analysis at the B3LYP/6-311++G(d,p) level.

Conformational Analysis

In a first step, all possible conformations of the metal−water clusters [$\mathrm{M(H_2O)}_n$; M = $\mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Be^{2+}}$, $\mathrm{Mg^{2+}}$ and $\mathrm{Ca^{2+}}$; $n = 1-6$] were explored to find the lowest energy conformers at the B3LYP/6-31G(d) level. Unless otherwise mentioned, the energies used for the discussion of conformations are taken from the B3LYP/6-31G(d) calculations. For $n = 2$, we tested four types of conformations (two W−M−W and two M−W−W; M = metal W = water) wherein the first two conformations possess D_{2d} and C_{2v} symmetry, whereas the other two have C_{2v} and C_s symmetry. Among four possible conformations, the W−M−W (D_{2d}) conformation is the lowest energy and is characterized as the minimum for all of the metal ions except M = $\mathrm{K^+}$ for which the structure with D_2 symmetry is the minimum. The conformation W−M−W with the C_{2v} symmetry is characterized as a first-order saddle point for all of the metal ions considered in this study. For $\mathrm{Ca^{2+}}$, the putative conformation M−W−W with C_s symmetry upon optimization yields a first-order saddle point, whereas similar putative conformations involving $\mathrm{Na^+}$, $\mathrm{K^+}$ and $\mathrm{Be^{2+}}$ ions invariably collapse to W-M-W type conformations upon optimization. The M−W−W conformations were obtained with C_s symmetry for M = $\mathrm{Li^+}$ and $\mathrm{Mg^{2+}}$. Expectedly, M−W−W structures are considerably less stable compared to W−M−W type structures.

For $n = 3$, three types of conformations were found; the first has the three water molecules directly attached to the metal ion. In this case, although the structures with different symmetries are possible, the structure with the D_3 point group is the minimum and is predicted to be the lowest energy for all trihydrated complexes except for **K-3W** and **Mg-3W** where they possess C_3 symmetry. The second and third conformations have two water molecules directly connected to the metal ion, and a third one interacts through hydrogen bonding with either of the former two. These two conformations are distinguished through the hydrogen bonding interaction of the third water molecule; one has bridge type hydrogen bonds (structure with C_{2v} symmetry) and the other contains single hydrogen bond (C_s symmetry). The bridging structures are less stable than the structures possessing only one hydrogen bond, as pointed out in earlier studies.[15] Out of these three conformations, the one in which all three water molecules directly bind with the metal ion exhibits the lowest energy on the M−3W potential energy surfaces; the second conformation (C_{2v}) is a first-order saddle point, and a third one is a higher-energy minimum with C_s symmetry.

In what follows, the label ($p + q$) will be used to denote the number of water molecules in the first (p) and second solvation shells (q). For the complexes with four water molecules, (4 + 0), (3 + 1), and (2 + 2) complexes are possible. In the case of complexes involving $\mathrm{Li^+}$ ion, the conformation of (4 + 0) type is about 4 kJ/mol more stable than (3 + 1) type and about 50−86 kJ/mol more stable than (2 + 2) complexes. Solvation of $\mathrm{Na^+}$ shows some interesting results by the B3LYP/6-31G(d) calculations; the (3 + 1) is isoenergetic to the (4 + 0) complex, and the same result is seen with the 6-31+G(d) and 6-311++G(d,p) basis sets. Conversely, the (4 + 0) is preferred over the (3 + 1) complex at the MP2(FULL)/6-31+G(d) level. In contrast to the results of Glendening et al.,[22] we observed that the (4 + 0) complex is about 9.2 kJ/mol more stable than the (3 + 1) complex for $\mathrm{K^+(H_2O)_4}$ at the MP2(FULL)/6-31+G(d) level. Our finding is in agreement with those reported by Kim and coworkers.[19b] For the tetrahydration of metal ions $\mathrm{Be^{2+}}$, $\mathrm{Mg^{2+}}$ and $\mathrm{Ca^{2+}}$, the (4 + 0) complex is more stable than (3 + 1) and (2 + 2) complexes, in agreement with previous theoretical studies.[15,18] The lowest energy structures of all the hydrated metal ions are depicted in Figures 1 and 2.

Three different types of complexes {(5 + 0), (4 + 1) and (3 + 2)} were generated for the pentahydrated metal ions. Among these, the (4 + 1) complex where four water molecules are directly coordinated to the metal ion and the fifth one through hydrogen bonding has the lowest energy on the potential energy surface for $\mathrm{Li^+}$, $\mathrm{Na^+}$ and $\mathrm{Be^{2+}}$. These three metal ions, which are of smaller size compared to the other three metal ions, do not accommodate the fifth water molecule in the first solvation shell due to “the crowding effect”. For pentahydrated $\mathrm{Mg^{2+}}$ and $\mathrm{Ca^{2+}}$, the (5 + 0) complexes with C_{2v} symmetry are found to be the global minima, which is in accordance with earlier theoretical studies.[15,18] It is worth mentioning that $\mathrm{K^+(H_2O)_5}$ has a different complex wherein four water molecules form a hydrogen bonding network and the metal ion binds to this water network along its centroid, and the fifth water molecule binds to $\mathrm{K^+}$ from the opposite side.

For $n = 6$, the possible complexes are (6 + 0), (5 + 1), (4 + 2) and (3 + 3). For $\mathrm{Ca^{2+}}$, the (6 + 0) complex is the most stable. The (4 + 2) complex has the lowest energy for hexahydrated $\mathrm{Mg^{2+}}$, $\mathrm{Li^+}$, $\mathrm{Na^+}$, and $\mathrm{K^+}$ ions. As we know from earlier studies on the solvation of $\mathrm{Mg^{2+}}$, it can accommodate six water molecules in its first solvation shell.[13,18,20] Therefore, we further refined geometries of the (4 + 2) and (6 + 0) complexes using the 6-31+G(d) and 6-311++G(d,p) basis sets with the B3LYP functional. The trend obtained using the 6-31+G(d) basis set is same as that for 6-31G(d). Similar to earlier studies,[13,18,20] the (6 + 0) complex is marginally (by 0.13 kJ/mol) more stable than the (4 + 2) complex at the B3LYP/6-311++G(d,p) level. The competing stability of (4 + 2) and (6 + 0) conformations of $\mathrm{Mg^{2+}(H_2O)_6}$ is in agreement with the presence of two distinct gas phase structures reported for hexahydrated $\mathrm{Mg^{2+}}$ ion.[13] Kim and co-workers reported that the (6 + 0) complex is somewhat less stable than the (4 + 2) complex for $\mathrm{K^+(H_2O)_6}$ at the MP2/TZ2P level.[19b] In contrast, the present study reveals that the (6 + 0) complex is about 17 kJ/mol more stable than (4 + 2) complex, indicating that $\mathrm{K^+}$ ion can also accommodate six water molecules in its first solvation shell. The hydration number of 6 predicted for $\mathrm{K^+}$ in the present study is in good agreement with the recent experimental report using neutron diffraction experiment of

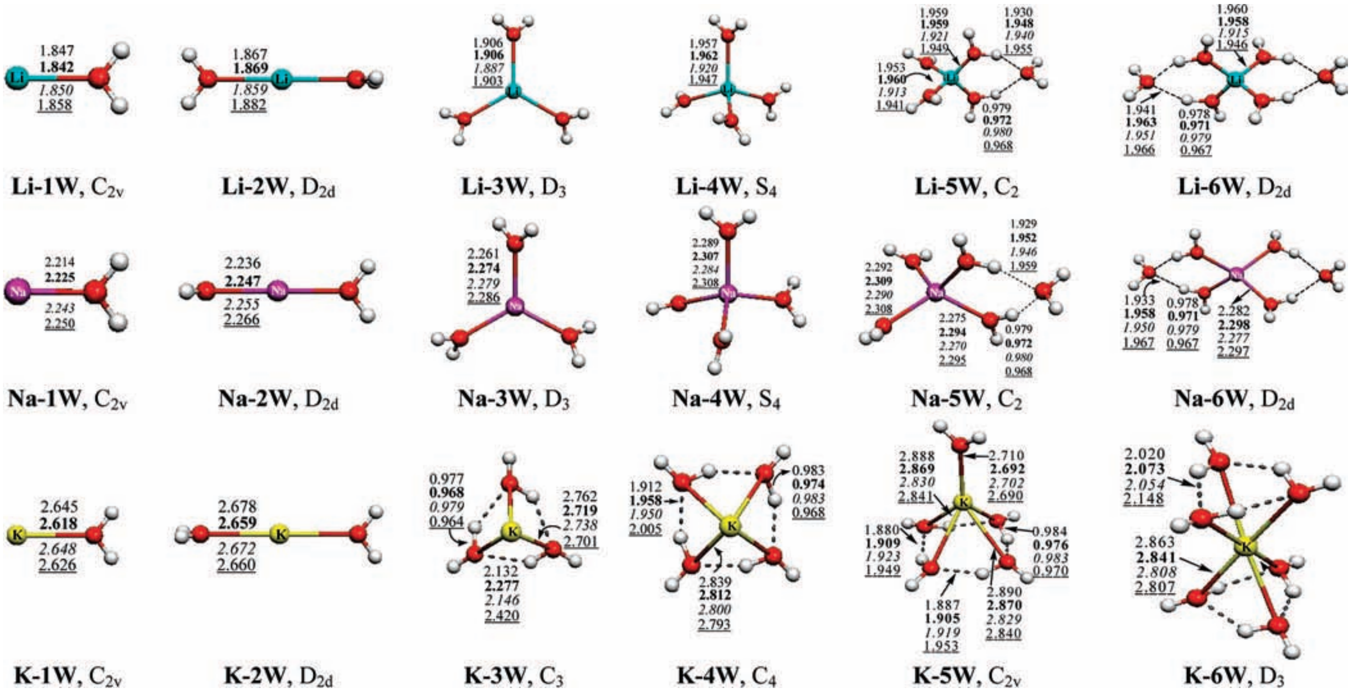


Figure 1. Optimized geometries of $M^+(H_2O)_n$ ($M^+ = Li^+$, Na^+ and K^+, $n = 1-6$) at B3LYP/6-31+G(d) (normal), B3LYP/6-311++G(d,p) (bold), MP2(FULL)/6-31+G(d) (italic) and MP2(FULL)/6-311++G(d,p) (underlined) levels of theory. All structures are minima on the potential energy surface. Bond lengths are given in Å.

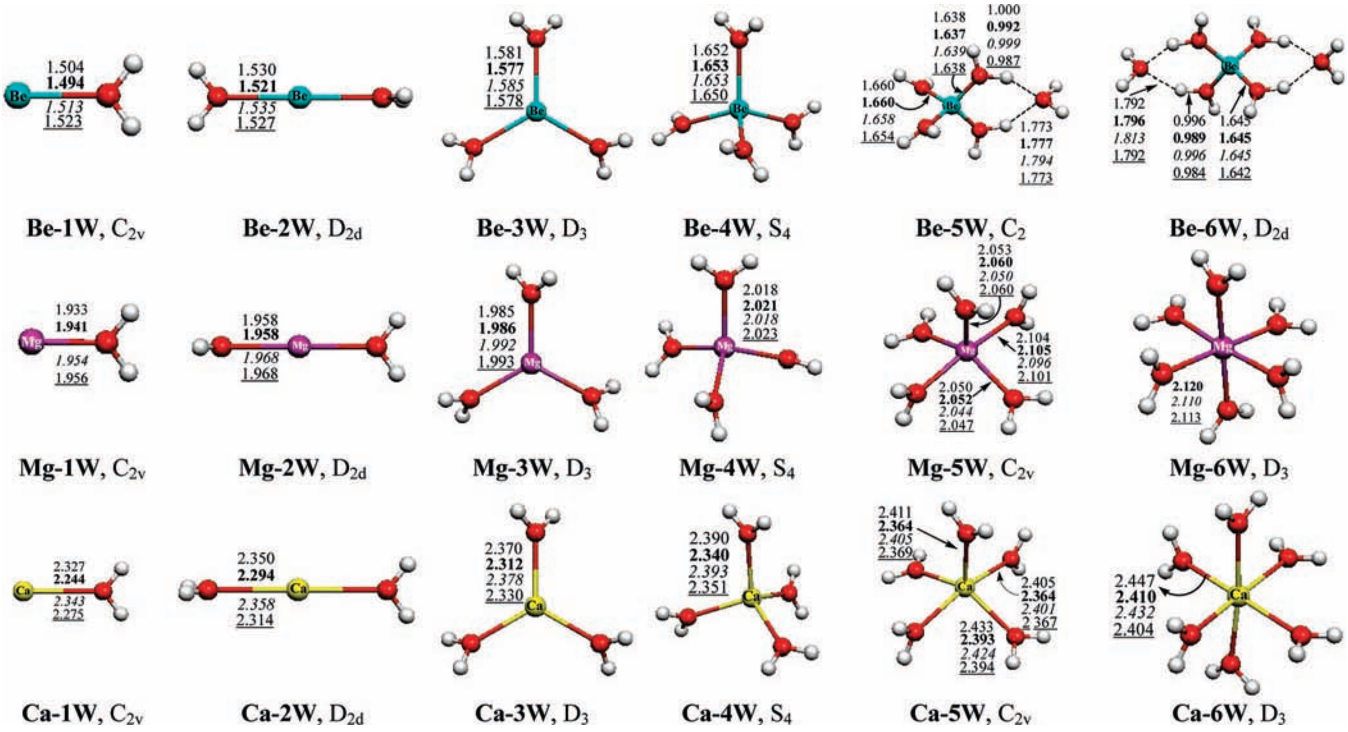


Figure 2. Optimized geometries of $M^{2+}(H_2O)_n$ ($M^{2+} = Be^{2+}$, Mg^{2+}, and Ca^{2+}, $n = 1-6$) at B3LYP/6-31+G(d) (normal), B3LYP/6-311++G(d,p) (bold), MP2(FULL)/6-31+G(d) (italic) and MP2(FULL)/6-311++G(d,p) (underlined) levels of theory. All structures are minima on the potential energy surface. Bond lengths are given in Å.

Soper et al.[8b] Geometrical parameters obtained at the B3LYP/6-31G(d) level for the complexes discussed above are available in the Supporting Information. The obtained lowest energy structures were further optimized at the B3LYP/6-31+G(d), MP2(FULL)/6-31+G(d), B3LYP/6-311++G(d,p) and MP2(FULL)/6-311++G(d,p) levels and the geometry parameters of these complexes are depicted in Figures 1 and 2. Thus, triple-ζ basis set with B3LYP or MP2 method is needed for proper identification of the lowest energy conformer of hydrated metal ions involving more than four water molecules.

The coordination number for almost all of these metal ions has been reported in the previous studies.[7,8,20−23,29] The solvation shell is completed with four water molecules for Li, Na and Be cations. For the addition of five and six water molecules, we have obtained (4 + 1) and (4 + 2) as the lowest energy complexes for the above-mentioned metal ions. This could be

TABLE 1: Sequential Binding Energy Values (kJ/mol) Calculated for $M^+(H_2O)_n$ Complexes (M = Li, Na and K) at Various Levels of Theory

		B3LYP				MP2(full)				CCSD(T)			
M^+	#W[a]	6-31+G(d)	6-311++G(d,p)	6-311++G(2d, 2p)[b]	6-311++G(3d,3p)[b]	6-31+G(d)[b]	6-311++G(d,p)[b]	6-311++G(2d, 2p)[b]	6-311++G(3d,3p)[b]	6-31+G(d)[b,d]	6-311++G(d,p)[b,d]	G3	exptl
Li^+	**1**	148.72	148.85	146.09	146.30	144.42	140.20	138.44	138.57	140.66	137.56	140.62	142.12[e] 137 ± 14[f]
	2	130.25	127.07	124.19	125.23	125.61	121.30	119.21	120.26	120.68	119.34	120.89	107.84[e] 114 ± 10[f]
	3	96.18	96.18	94.93	94.22	97.39	95.68	95.60	95.22	95.97	94.51	93.51	86.53[e] 94 ± 4[f]
	4	66.46	65.00	64.46	64.33	70.22	67.59	68.80	69.35	68.30	67.59	70.47	68.55[e] 71 ± 5[f]
	5	60.99	59.27	56.39	56.39	59.31	55.51	57.27	58.10	56.60	54.42	52.17	58.10[e] 60 ± 4[f]
	6	57.27	55.34	52.75	52.79	55.43	52.29	53.80	54.47	52.79	51.37	45.19	50.58[e] 63 ± 5[f]
	AD[c]	**8.40**	**7.52**	**6.10**	**6.23**	**6.44**	**4.97**	**4.72**	**4.89**	**4.64**	**4.93**	**5.81**	
Na^+	**1**	105.84	104.21	100.99	101.20	102.16	97.23	95.51	96.68	98.90	93.97	102.03	100.32[e] 94.5 ± 7.5[g]
	2	93.13	92.67	89.41	89.91	90.25	87.53	85.40	86.65	86.48	83.98	88.37	82.76[e] 81.9 ± 5.9[g]
	3	77.66	76.70	74.32	73.61	76.87	74.32	73.19	73.32	72.94	70.39	74.74	66.04[e] 70.2 ± 5.9[g]
	4	62.24	61.03	58.52	58.60	61.53	60.61	59.86	60.69	54.80	56.22	65.04	57.68[e] 54.8 ± 5.9[g]
	5	56.26	57.10	54.63	54.84	56.22	52.25	54.34	55.30	53.80	50.66	49.53	51.41[e]
	6	56.01	54.72	52.12	52.08	54.42	50.95	53.09	53.80	51.96	50.24	50.24	44.73[e]
	AD[c]	**8.03**	**7.23**	**4.51**	**4.56**	**6.44**	**4.35**	**4.68**	**5.14**	**4.10**	**3.26**	**5.14**	
K^+	**1**	77.25	76.83	72.31	71.94	76.66	74.65	71.14	71.44	75.95	73.11	69.72	74.82[e]
	2	68.22	67.55	63.37	62.95	68.43	66.59	63.45	63.58	67.84	65.42	62.74	67.30[e]
	3	65.29	56.10	48.74	48.40	56.05	49.66	54.01	55.72	54.97	48.32	48.32	55.18[e]
	4	64.66	51.41	54.21	54.51	57.10	51.50	53.30	54.30	54.13	49.45	50.91	49.32[e]
	5	43.26	54.97	51.33	51.04	55.34	53.67	51.92	51.79	54.42	52.58	52.33	44.73[e]
	6	41.67	38.96	37.83	37.03	47.82	42.59	44.35	45.19	48.28	42.18	39.54	41.80[e]
	AD[c]	**5.06**	**3.05**	**4.72**	**5.06**	**4.72**	**3.05**	**3.72**	**3.85**	**3.80**	**3.14**	**4.68**	

[a] Number of water molecules bound with metal ions. [b] Single point calculations on B3LYP/6-311++G(d,p) optimized geometries. [c] Average deviation with respect to the experimental value from ref 19. [d] BSSE corrections for CCSD(T) calculations are taken from MP2 method. [e] Taken from ref 9. [f] Taken from ref 14. [g] Taken from ref 10a.

explained by steric effects when more than four water molecules are directly attached to the smaller metal ions. Hydration of K^+ merits special mention here because the solvation is completely different and unique from all other metal−$(H_2O)_n$ complexes (particularly $n \geq 3$) considered in this study. Water−water interactions exist through hydrogen bonding despite the water molecules being directly bonded to the metal ion in $K^+(H_2O)_{3-6}$ complexes. In the case of the $K^+(H_2O)_3$ complex, the potassium ion is at the centroid of the hydrogen bonding network formed by three water molecules. As shown in Figure 1, the addition of six water molecules directly connecting to K^+ ion gives rise to a double-cone-like structure owing to the presence of hydrogen bonding among the water molecules. Except for K^+, all other metal cations give complexes having D_3 and S_4 symmetry when three and four water molecules are added, respectively, whereas the K^+ gives complexes having C_3 and C_4 symmetry. The metal ions Mg^{2+} and Ca^{2+} can accommodate six water molecules in their first solvation shell.

Geometries. The M−O distance in $M^+(H_2O)$ (M = Li, Na, and K) complexes gradually increases with the number of water molecules in the complex. Although an increase is expected, the variation in the M−O distances between the MP2 and B3LYP methods is notable. The Li−O distance in the $Li^+(H_2O)$ complex is longer at the MP2 method than at the B3LYP level with all basis sets considered, whereas, in $Li^+(H_2O)_n$ ($n = 3-6$), B3LYP predicts a longer Li−O distance than MP2 does. Although Li−O distance for the **Li-2W** complex is longer at the B3LYP/6-31+G(d) level compared to MP2(FULL)/6-31+G(d) level, the B3LYP/6-311++G(d,p) level predicts slightly shorter (0.01 Å) Li−O distance compared to MP2(FULL)/6-311++G(d,p) level. The increase of Li−O distance from **Li-1W** to **Li-2W** at the MP2/6-31+G(d) level is less compared to other levels considered. The short Li−O distance obtained at the MP2/6-31+G(d) level for **Li-2W** could result in the repulsive interactions between the closed-shell core electrons on the metal ion and the closed-shell ligand. To relieve such repulsive interactions, Rodgers and Armentrout suggested employing the basis functions that properly treat the core electrons. Further, they revealed that the core correlation on the lithium ion is needed to polarize its core electrons away from the ligand and to correlate with the ligand electrons.[45] In the case of water solvation of alkali metal ions, the increase of the M−O distance at B3LYP is higher than MP2 method upon the addition of each water molecule. For example, in the sodium complexes, the Na−O distance in $Na^+(H_2O)$ is 0.025 Å longer by MP2(FULL)/6-311++G(d,p) than by B3LYP/6-311++G(d,p) level, but **Na-4W**, **Na-5W** and **Na-6W** complexes exhibit very similar Na−O distances by both methods. The K−O distance increases as successive water molecules are added (up to $n = 5$), but it decreases when the sixth water molecule is added to K^+. This is an interesting trend compared to all other metal ion hydrations considered here. The structure of **K-5W** is a “tetragonal pyramidal” shape possessing cyclic water tetramer with four H-bonded molecules and the fifth water molecule binds with the K^+ ion without involving any H-bond.

TABLE 2: Sequential Binding Energy Values (kJ/mol) Calculated for $M^{2+}(H_2O)_n$ Complexes (M = Be, Mg and Ca) at Various Levels of Theory

		B3LYP				MP2(full)				CCSD(T)		
M^{2+}	#W[a]	6-31+ G(d)	6-311++ G(d,p)	6-311++ G(2d, 2p)[b]	6-311++ G(3d,3p)[b]	6-31+ G(d)[b]	6-311++ G(d,p)[b]	6-311++ G(2d, 2p)[b]	6-311++ G(3d,3p)[b]	6-31+ G(d)[b,d]	6-311++ G(d,p)[b,d]	G3
Be^{2+}	**1**	613.62	610.49	616.13	616.97	591.05	576.71	585.58	586.79	588.13	573.29	595.19
	2	499.05	493.03	499.09	501.52	487.39	481.79	483.21	484.92	486.59	480.45	487.97
	3	327.38	319.18	322.78	322.49	326.46	315.05	322.70	322.91	325.75	314.92	325.96
	4	203.19	197.71	197.96	197.09	208.71	200.43	205.20	204.90	207.79	200.22	208.04
	5	131.75	129.83	125.99	126.99	126.49	121.72	123.56	125.69	123.14	119.92	119.00
	6	124.10	121.93	118.09	119.00	120.01	115.08	116.58	118.34	117.08	113.32	113.82
	AD[c]	**9.80**	**9.41**	**9.45**	**10.49**	**3.26**	**7.86**	**4.64**	**4.81**	**2.72**	**8.28**	
Mg^{2+}	**1**	343.26	339.92	342.09	345.10	326.92	317.51	322.70	327.59	321.86	313.79	335.95
	2	302.51	302.59	301.88	302.59	291.72	286.71	288.46	290.59	287.54	283.45	297.28
	3	243.61	240.02	240.31	241.40	241.23	233.54	235.92	238.22	236.63	232.28	237.22
	4	193.37	191.24	190.11	190.69	195.54	190.02	191.61	193.24	190.73	189.40	196.13
	5	126.49	127.16	124.48	125.36	131.54	130.79	131.50	132.26	129.58	130.08	134.51
	6	105.21	96.73	97.23	98.69	101.66	103.08	102.74	104.33	100.95	102.91	111.40
	AD[c]	**5.98**	**6.52**	**7.36**	**7.65**	**5.31**	**8.49**	**6.60**	**4.72**	**7.52**	**10.12**	
Ca^{2+}	**1**	223.09	242.27	238.30	241.14	212.64	223.38	221.50	225.51	211.22	220.12	224.13
	2	202.40	206.99	201.02	202.14	198.55	198.34	194.58	196.92	197.71	195.92	197.67
	3	180.20	186.64	182.54	184.42	176.48	179.28	177.69	179.95	175.85	177.27	176.02
	4	157.38	158.80	154.91	154.74	157.84	156.71	154.79	156.04	157.75	155.45	155.08
	5	125.36	124.19	120.05	120.34	130.21	127.28	126.49	128.03	130.96	126.74	128.45
	6	101.45	98.56	96.31	96.68	107.59	104.50	104.58	105.84	108.43	104.42	110.14
	AD[c]	**4.01**	**9.61**	**7.73**	**8.65**	**3.30**	**2.17**	**2.55**	**1.96**	**3.34**	**2.47**	

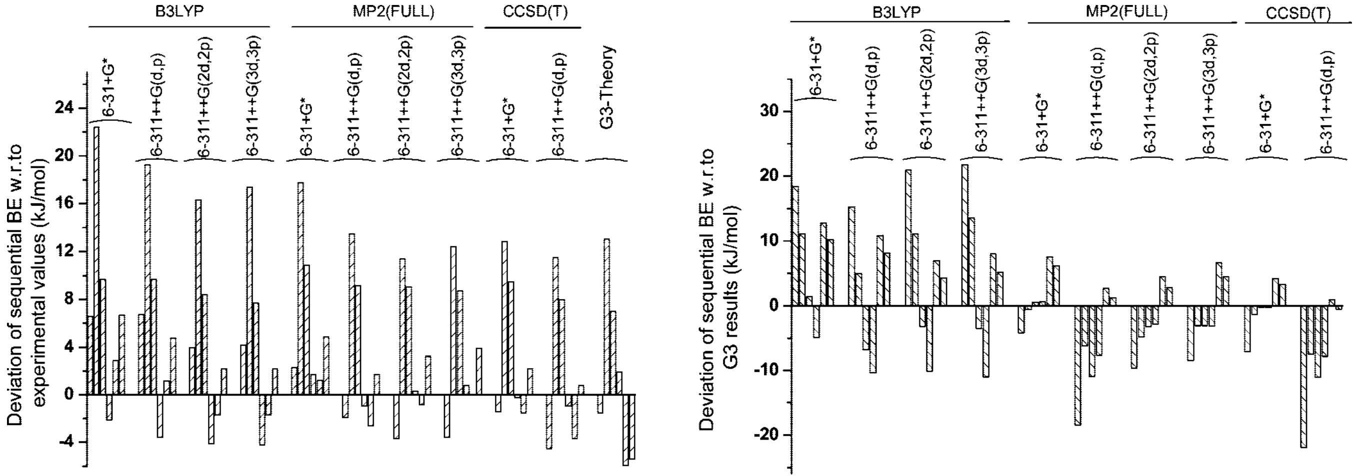
[a] Number of water molecules bound with metal ions. [b] Single point calculations on B3LYP/6-311++G(d,p) optimized geometries. [c] Average deviation with respect to the results of G3 theory. [d] BSSE corrections for CCSD(T) calculations are taken from MP2 method.

In this structure, the K−O distance of the fifth water molecule is considerably shorter than that for the water molecules connected through the H-bonds. The latter K−O distance is the longest in $K^+(H_2O)_{n=1-6}$ complexes, and the former K−O distance is longer than that in **K-1W** and **K-2W** complexes.

The M−O distances in $M^{2+}(H_2O)_{n=1-3}$ (M = Be, Mg, and Ca) are predicted to be longer by MP2 than by B3LYP, whereas they are comparable for $M^{2+}(H_2O)_{n=4-6}$ (M = Be and Mg) complexes. Three different M−O distances are obtained for $M^{2+}(H_2O)_5$ (M = Mg and Ca) complexes. Unlike the complexes involving other metal ions, the Ca−O distances in Ca^{2+} hydrated complexes are considerably affected by the basis set both by B3LYP and by MP2. Double-ζ basis set yields substantially longer Ca−O distances compared to triple-ζ basis sets in $Ca^{2+}(H_2O)_n$ complexes. We also scrutinized the hydrogen bonding distances at various levels of theory. Generally, hydrogen bond lengths increase as the quality of basis set increases for $M(H_2O)_{n=5,6}$ (M = Li^+ and Na^+) complexes both by B3LYP and by MP2 methods. As the number of water molecule increases in the second solvation shell, the hydrogen bond length also increases with a concomitant decrease of the bond length of O−H bond that is involved in H-bonding in the case of $M(H_2O)_{n=5,6}$ (M = Li^+, Na^+ and Be^{2+}). The hydrogen bond lengths in $K^+(H_2O)_n$ complexes decrease for $n = 3-5$ and again increase for $n = 6$. In this case, the hydrogen bond lengths depend on the number of water molecules present in the hydrogen bonding network.[19b,22] If the number of water molecules is fewer, the hydrogen bond lengths are long. The structures **K-3W** and **K-6W** possessing tripod-like arrangements in their hydrogen bonding network (three water molecules involved) exhibit longer hydrogen bond length compared to **K-4W** and **K-5W**, which appear as square pyramid-like shape with four water molecules in the hydrogen bonding network.

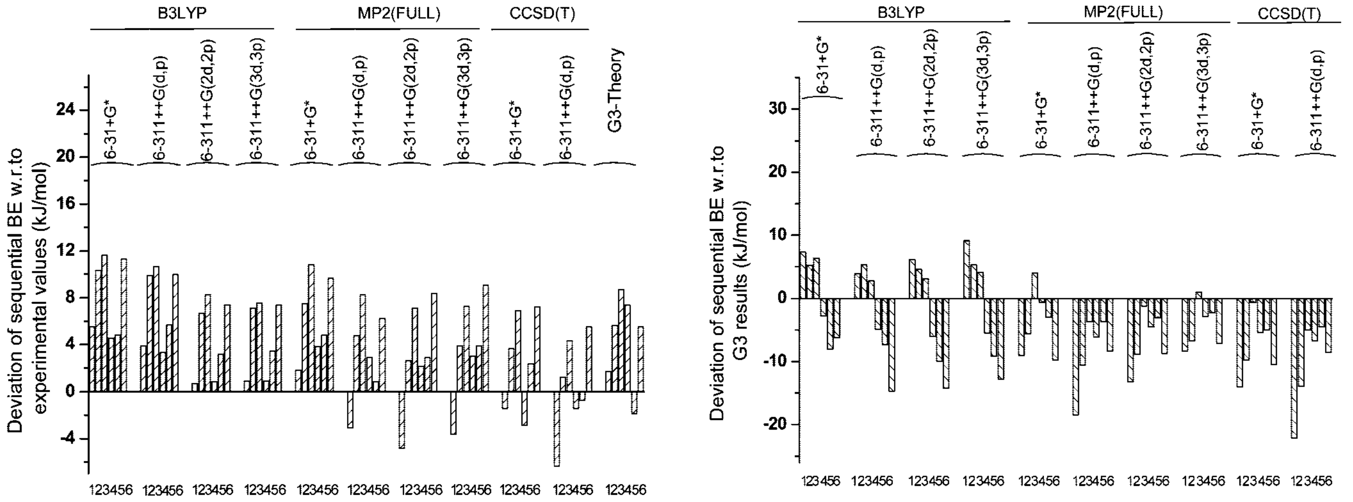
Energetics. Tables 1 and 2 list the BSSE corrected sequential binding energies (kJ/mol) calculated at various levels of theory. Irrespective of the geometries used, we could observe that the sequential binding energy trends are identical. For the current discussion, we have taken the results obtained using B3LYP/6-311++G(d,p) level optimized geometries, and the results obtained using MP2/6-311++G(d,p) optimized geometries are provided in the Supporting Information (Tables S1 and S2). When we compare the sequential binding energies obtained using MP2 and B3LYP geometries, except for Be^{2+} the MP2 binding energies are slightly better (0.5−1.5 kJ/mol closer to experimental values) than B3LYP values. We have compared the calculated sequential binding energies of hydration of Li^+, Na^+ and K^+ with experimental data available in the literature.[9,10a,14] Figure 3 shows the schematic representation of the performance of different methods and basis sets for the sequential binding energies. In this figure, for the sake of uniformity, we have taken the experimental results of Dzidic et al.[9] for the alkali metal ions as the reference values for obtaining the deviation of sequential binding energies. From Tables 1 and 2, it is clear that, with few exceptions upon addition of each water molecule to metal ion, the incremental binding energies gradually decrease. Generally, our results are in good agreement with the experimental results of Dzidic et al.,[9] Dalleska et al.,[10b] and Rodgers et al.[10a,14] A closer look at the data given in Table 1 reveals that the sequential binding energies for $K^+(H_2O)_n$ do not always decrease as the number of water molecules increase, although the reported experimental values gradually decrease.[9] It should be noted that, for $K^+(H_2O)_n$ complexes, the sequential binding energies range from 77.3 to 37.6 kJ/mol, which is the lowest among the series of metal−water complexes considered in this study.

From Figure 3, we could see a clear trend for sequential binding energies at various levels of theory. For alkali metal cations, MP2 and CCSD(T) perform consistently well with both double- and triple-ζ basis sets (~6.5 kJ/mol average deviation from experimental results). When the B3LYP functional is selected for calculating the sequential binding energies, we recommend the 6-311++G(2d,2p) basis set for the Li^+ and Na^+, and the 6-311++G(d,p) basis set for the K^+ ion. Rodgers and Armentrout reported the sequential binding energy values for



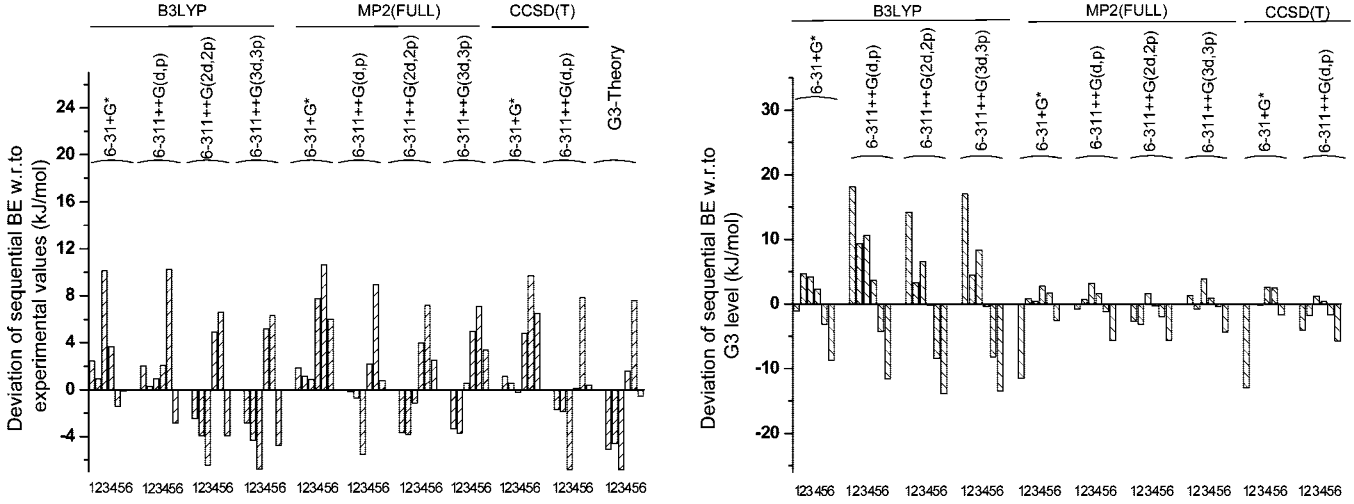
(a) $Li^+(H_2O)_n$; n=1-6

(d) $Be^{2+}(H_2O)_n$; n=1-6



(b) $Na^+(H_2O)_n$; n=1-6

(e) $Mg^{2+}(H_2O)_n$; n=1-6



(c) $K^+(H_2O)_n$; n=1-6

(f) $Ca^{2+}(H_2O)_n$; n=1-6

Figure 3. Deviation of sequential binding energy (SBE) with respect to experimental results (for alkali metal hydration) or G3 theory (for alkaline earth metal hydration).

$Li^+(H_2O)_n$ ($n = 1-6$). In the case of $n = 2$, 3 and 6, a large discrepancy of sequential binding energies is observed between the experimental results of Rodgers et al.[14] and Dzidic et al.[9] In particular, an increase of the sequential binding energy, which is not supported by current theoretical study, is observed by Armentrout and co-workers when a sixth water molecule is added to the Li^+ ion. On the other hand, Figure 3a shows a large deviation of the calculated sequential binding energies for

$Li^+(H_2O)_2$ and $Li^+(H_2O)_3$ with respect to the experimental values of Dzidic et al.,[9] irrespective of the method and basis set. It is worth remarking that the calculated values for the $Li^+(H_2O)_2$ and $Li^+(H_2O)_3$ are in very good agreement with the experimental numbers of Armentrout and co-workers[14] and do not support the experimental results of Dzidic et al.[9] reported nearly four decades ago. As shown in Table 1, the experimental results of sequential binding energies for $Na^+(H_2O)_{n=1-4}$ reported by Rodgers et al.[14] are in agreement with those of Dzidic et al.[9]

In the case of Be^{2+}, Mg^{2+}, and Ca^{2+}, as no experimental values are available, we compare the calculated results with those obtained by the high level G3 method. For these alkaline earth metal ions, the performance of MP2 and CCSD(T) seems to be promising with an average deviation of 2−10 kJ/mol. Experimental results for sequential binding energies of $M^{2+}(H_2O)_n$; (M = Mg, Ca) are only available in the literature for $n = 5$ and 6.[10b,12−15] In the case of $Ca^{2+}(H_2O)_6$, three different sequential binding energies of 91 ± 5 (Carl et al.),[15] 92 ± 3 (Rodriguez-Cruz et al.),[13b] 106 ± 4 (Peschke et al.)[10b] were reported. Our computational results at the G3, CCSD(T) and MP2 levels are in very good agreement with the value reported by Peschke et al.[10b] Furthermore, depending on the level of theory, the calculated values deviate by 8−21 kJ/mol from the other experimental values.[13b,15] Values of 112 and 115 kJ/mol were reported for the binding energy of the last water molecule in $Ca^{2+}(H_2O)_5$.[13b,15] For this complex, the computed results at different levels are comparable to the experimental numbers. The sequential binding energies obtained for $Mg^{2+}(H_2O)_6$ at different levels (Table 2) are in good agreement with the experimental result of 98.2 ± 6.7 kJ/mol, reported by Williams and co-workers using a BIRD experiment.[13a] Calculations at different levels yield 124−134 kJ/mol for the sequential binding energy of $Mg^{2+}(H_2O)_5$, and the experimental value was reported as 106.6 ± 5.4 kJ/mol.[13b] The sequential binding energy difference between $Mg^{2+}(H_2O)_5$ and $Mg^{2+}(H_2O)_6$ is 8 ± 6 kJ/mol for experiment but it is 20−30 kJ/mol for theory.

The sequential binding energies for $Be^{2+}(H_2O)_n$ complexes merit special mention. They are the highest among various metal ion−water clusters investigated in this study. The magnitude of the decrease in sequential binding energies is substantially higher in $Be^{2+}(H_2O)_n$ as "*n*" increase from 1 to 5. Inspection of the data in Table 2 shows that the sequential binding energy of $Be^{2+}(H_2O)_5$ is lower than that of $Mg^{2+}(H_2O)_5$ and $Ca^{2+}(H_2O)_5$ at the MP2, CCSD(T) and G3 levels. This can be attributed to the addition of fifth water molecule to the second hydration shell in the $Be^{2+}(H_2O)_5$ complex where the dispersion interaction occurs. It is important to mention that the B3LYP functional does not produce the above-mentioned trend of sequential binding energy for the complexes involving five water molecules as the high level ab initio methods do. The B3LYP functional underestimates the sequential binding energy for $Be^{2+}(H_2O)_5$ complex because it does not properly treat the dispersion interactions. For the solvation of metal ions where the dispersion interactions occur, as shown in the recent reviews,[28] newly developed hybrid meta functionals by Truhlar and co-workers[28a] and double-hybrid density functional (B2PLYP-D) of Grimme and co-workers[28b] could be employed to obtain the results with good accuracy as high-level ab initio methods but with less computational cost. Figure 3 illustrates the very good performance of the MP2(FULL)/6-31+G(d) level in calculating sequential binding energies of $Be^{2+}(H_2O)_n$ and $Mg^{2+}(H_2O)_n$ complexes. It is worth noting that for both $Be^{2+}(H_2O)_n$ and $Ca^{2+}(H_2O)_n$ complexes, the MP2 method is much better than B3LYP functional in predicting the sequential binding energies. The current study provides geometries at high-level of theory and energetics at a high-level ab initio and G3 methods. Hence, this study will be beneficial for the development of potential functions and also to validate the existing force fields. The results obtained using G3 theory may serve as a reliable reference in cases where experimental data are not available.

TABLE 3: Reorganization Energy (kJ/mol) Calculated at the B3LYP/6-311++G(d,p) and Level

# W[a]	B3LYP/6-311++G(d,p)					
	Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Ca^{2+}
2	30.18	26.38	24.66	43.47	31.43	27.59
3	94.64	84.14	41.84	124.65	93.72	84.52
4	173.47	154.33	46.94	223.80	171.09	154.37
5	197.76	175.73	84.48	273.04	244.20	217.11
6	224.55	193.62	119.30	318.73	311.87	280.69

[a] Number of water molecules bound with metal ions.

The BSSE corrected total binding energies at various levels of theory are listed in Tables S3 and S4 in the Supporting Information. Irrespective of the geometries used, we could observe that the total binding energy (BE) trends are identical (Tables S5 and S6). As expected, the total binding energy increases as the number of water molecules increases for each of the metal ions. The total binding energies for the hydration of the doubly charged alkaline earth metal ions are 3−3.5 times larger than those for the singly charged alkali metal ion in the same row of the periodic table. The affinity for water molecules follows the trend $Be^{2+} > Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$. Taking the total binding energies obtained at the G3 method as reference values, we compared the total binding energies obtained at various levels of theory. Figure S7 (see Supporting Information) depicts the deviation of total binding energies at each of the level employed with respect to the G3 results. Changing the quality of basis set and method showed its consequences in several ways (see Figure S7). Unlike the sequential binding energies, there are no regular trends to put forward here. Hence, the results are provided in the Supporting Information.

We also calculated the reorganization energy of water clusters by taking the energy difference between a "pure" water cluster and the framework of water cluster in the metal−water complexes, at the B3LYP and MP2 methods with the 6-311++G(d,p) basis set. Because we observed similar trends by B3LYP and MP2, the analysis is performed only at the B3LYP level; the results of MP2 are available in the Supporting Information. The reorganization energies obtained at the B3LYP functional are provided in Table 3 and the correlation graph of reorganization energy with the size of water clusters are shown in Figure 4. As the metal ion approaches, all water molecules are reorganized in a different fashion and this reaction is an endothermic process for all water clusters. The reorganization of water cluster containing two waters is about 3 times lower than that of one containing three water molecules. Except for the K^+ ion, the above observation is true for all metal ions. It is observed that, as the size of metal ion increases, the reorganization energy decreases. If we look at the K^+−water complexes, the increase in the reorganization energy is not as high as for the other metal ions in the current study.

Charge Analysis. NPA charges were calculated by the B3LYP and MP2 methods with the 6-311++G(d,p) basis set. The values obtained by the B3LYP are listed in Table 4, and

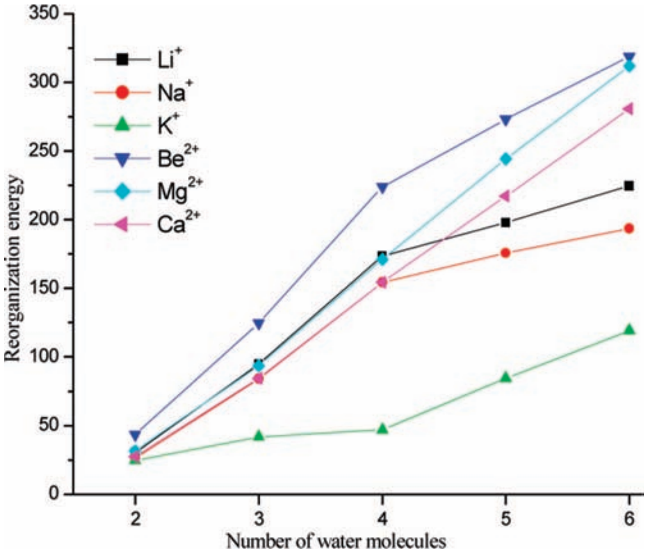


Figure 4. Correlation of number of water molecules versus reorganization energy at the B3LYP/6-311++G(d,p) level.

TABLE 4: NPA Charges (in e⁻) on Metal Ions of the Considered Complexes at the B3LYP/6-311++G(d,p) Level

# W^a	Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Ca^{2+}
1	0.992	0.996	0.997	1.921	1.961	1.963
2	0.970	0.986	0.994	1.787	1.912	1.947
3	0.942	0.972	0.990	1.736	1.873	1.915
4	0.915	0.955	0.986	1.712	1.843	1.888
5	0.914	0.954	0.980	1.710	1.834	1.876
6	0.914	0.954	0.973	1.710	1.840	1.862

[a] Number of water molecules bound with metal ions.

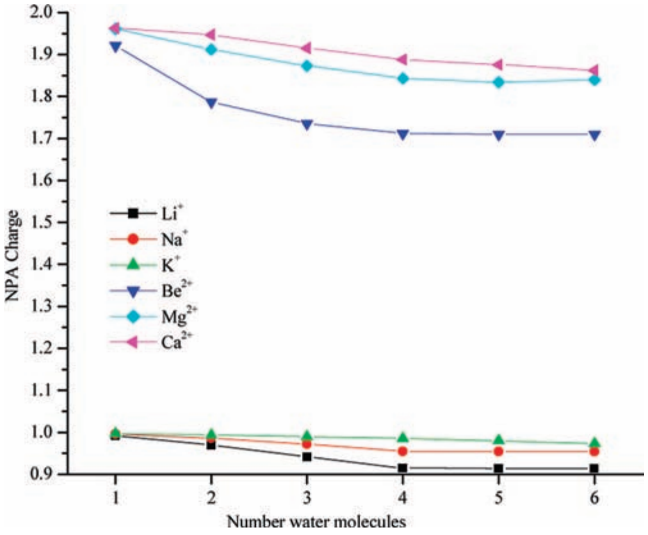


Figure 5. Correlation of number of water molecules in metal−water clusters versus NPA charges of the metal ions in the complexes at the B3LYP/6-311++G(d,p) level.

those obtained by the MP2 method are given in the Supporting Information. A plot of metal ion charge in the complexes versus size of metal−water clusters is depicted in Figure 5. A quick perusal of the charge transfer phenomenon on metal ions shows that the charge on metal ions monotonically decreases as the number of water molecules increases in the metal−water cluster.

Conclusions

The paper provides geometries at high-level of theory and energetics at the high-level ab initio and G3 methods for the hydration of alkali (Li^+, Na^+ and K^+) and alkaline earth metal ions (Be^{2+}, Mg^{2+} and Ca^{2+}). The following conclusions can be drawn from the current study:

(1) The present study suggests triple-ζ basis set with B3LYP or MP2 method for correct identification of the lowest energy conformer of hydrated metal ions involving more than four water molecules.

(2) No single level (at B3LYP and MP2) is found to consistently show excellent performance for the hydration of all the metal ions considered in this study.

(3) We observed a clear trend for sequential binding energies at various levels of theory. For alkali metal cations, MP2 and CCSD(T) perform consistently well with both double- and triple-ζ basis sets (~6.5 kJ/mol average deviation from experimental results). The performance of MP2 and CCSD(T) seems to be promising with an average deviation of 2−10 kJ/mol for alkaline earth metal ions, and MP2(FULL)/6-31+G(d) is found to be reliable.

(4) For both $Be^{2+}(H_2O)_n$ and $Ca^{2+}(H_2O)_n$ complexes, the MP2 method shows much better agreement with G3 compared to B3LYP functional. Considering the fact that experimental values are unavailable, validation of the performance of these routine levels of theory is not straightforward. Thus, to the extent possible more accurate levels of theory has to be applied for the second row metals.

(5) Upon addition of each water molecule, the variation in the M-O distance is higher by B3LYP than by MP2 method.

(6) As the size of metal−water cluster increases, the charge on metal ion decreases monotonically.

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Supporting Information Available: Geometrical parameters of all conformations explored at the B3LYP/6-31G(d) level, total binding energies calculated at various levels using the B3LYP/6-311++G(d,p) and MP2(FULL)/6-311++G(d,p) optimized geometries, sequential binding energies calculated using the MP2(FULL)/6-311++G(d,p) optimized geometries, reorganization energies obtained at the MP2(FULL)/6-311++G(d,p) level, ZPVE values for all conformations obtained at the B3LYP/6-31G(d) level, and NPA charges obtained at the MP2(FULL)/6-311++G(d,p) level. This material is available free of charge via Internet at http://pubs.acs.org.

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