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# Insights into the Structures, Energetics, and Vibrations of Monovalent Cation–(Water)<sub>1–6</sub> Clusters<sup>†</sup>

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This study details the interactions prevailing in aqueous clusters of monovalent alkali metal, ammonium, and hydronium cations. The calculations involve a detailed evaluation of the structures, thermodynamic energies, and IR spectra of several plausible conformers of  $M^+ \cdot (H_2O)_{1-6}$  ( $M = Li, Na, K, Rb, Cs, NH_4, H_3O$ ) clusters at the second-order Møller–Plesset (MP2) and density functional levels of theory. A detailed decomposition of the interaction energies has been carried out for complexes involving one or two water molecules using symmetry adapted perturbation theory. Some of the salient insights on the structures include the emergence of the second solvent shell even before the realization of the maximal coordination number of the cation. This effect was more pronounced in clusters involving the larger cations. The quantitative estimates of various components of the interaction energy indicate the predominance of electrostatic energies in the binding of these cations to water molecules. Interestingly, for all the hydrated alkali metal cation complexes, the contribution of electrostatic energy is almost the same as the total attractive interaction energy, whereas the sum of the induction and dispersion energies are almost canceled out by exchange–repulsion energy. However, the contribution of dispersion energies slowly starts increasing as the size of the cation increases and is quite substantial in case of the  $Cs^+$  complexes. In the organic cations, the dispersion energies become significant, though not comparable to the electrostatic energies. In addition to the evaluation of the harmonic frequencies of –OH stretching mode of all the structures, the anharmonic frequencies were evaluated for the smaller clusters. As the size of the cation and the size of the water cluster increases, the red shifts associated with the –OH stretching mode progressively become larger for the alkali metal cation containing complexes. For the organic cation ( $NH_4^+, H_3O^+$ ) containing complexes, an opposite trend is observed. Compared to the isolated water monomer, the ratio of the infrared intensities of the asymmetric and symmetric –OH stretching modes is very small. However, this ratio progressively becomes larger as the size of the cation increases.

## Introduction

An understanding of the nature of ions in solution is one of the fundamental aspects of contemporary chemistry and biology. In this connection, a large number of experimental and theoretical studies have been carried out on the solvation of cations in both the condensed and gas phases.<sup>1–12</sup> Investigations in the gas phase have, in particular, been very useful in obtaining valuable insights into the modulation of the properties of cation–water clusters, as a result of an incremental addition of water molecules.<sup>1–7,12</sup>

Starting from the pioneering work of Kebabian and co-workers, a wealth of experimental data is available on thermodynamic properties of small monovalent cation–water clusters.<sup>3–6,13–18</sup> Thus the magnitudes of the experimental enthalpies indicate that the smaller cations bind water more strongly than larger cations, and the attachment of water molecules progressively becomes

more facile as the size of the ionic cluster increases. The latter observation indicates that specific ion–solvent interactions are significant only in the first solvation steps. Beyond a certain size of the cationic water cluster  $\{M^+ \cdot (H_2O)_{m=6-8}\}$ , the cumulative clustering enthalpies approach the differential bulk solvation enthalpies.<sup>18</sup>

More recently, the endeavors of Lisy and co-workers on the vibrational features of these ionic clusters yielded valuable insights into their structures.<sup>1,19,20</sup> Thus vibrational features indicating the presence of hydrogen bonding between adjacent water molecules are observed in the  $Cs^+ \cdot (H_2O)_3$  complex.<sup>19</sup> These results indicate the development of a secondary solvent shell prior to what might be considered as the optimum coordination number has been attained for the primary shell. Additionally, they also observe that the addition of a single  $Cs^+$  cation to a single water molecule  $Cs^+ \cdot (H_2O)_1$  leads to a dramatic decrease in the ratio of the vibrational intensities of the asymmetric and symmetric O–H stretches of water.

On the theoretical front, several studies have reported the structures, energetics, and vibrational frequencies of these cation–water clusters.<sup>12,21–40</sup> Early work by Clementi and co-workers provided much information about the energetics and structures of microclusters.<sup>21</sup> The information, which included

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the effect of temperature, indicated that the pair additive approximations were quite substantial for these small complexes. The advent of fast computers and the accompanying developments in *ab initio* correlated methodologies revolutionized the theoretical description of these cationic water clusters. Apart from the evaluation of structures of small-sized cationic water clusters, several groups have obtained fairly accurate estimates of the interaction enthalpies.<sup>24–31</sup> However, a question that most theoretical groups have sought to answer is how the solvent molecules build up about the cation in distinct shells. Though it is well-known that a certain number of solvent molecules attach intimately to the core cation, the reasons for the formation of a new solvent shell are not very clear. Though early theoretical investigations have conjectured that steric repulsions promote the formation of the secondary solvent shell, it was noted in an earlier study from our group that entropy effects cause the  $C_1$  form of  $\text{Na}^+(\text{H}_2\text{O})_6$  (five waters are coordinated to the  $\text{Na}^+$  cation in the primary shell) to be more preferred over the  $D_{2d}$  form (only four waters are coordinated to the  $\text{Na}^+$  cation in the primary shell) at room temperature.<sup>30</sup>

In previous studies from our group, the structures and energetics of small-sized water clusters of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ag}^+$  cations were evaluated using *ab initio* methods.<sup>27–31,40</sup> Apart from providing a good agreement of the calculated and experimentally determined enthalpies, the calculations on the  $\text{K}^+(\text{H}_2\text{O})_{1–6}$  clusters yielded interesting insights into coordination numbers and the corresponding energetic stabilities. Thus, in the penta- and hexa-hydrated clusters, relatively small energetic differences existed between structures exhibiting cation coordination numbers of 4, 5, and 6. The recent calculations on  $\text{Ag}^+(\text{H}_2\text{O})_{1–6}$  clusters highlighted the role of theoretical methodology in the evaluation of coordination numbers.<sup>40</sup> Thus, although calculations using the second-order Møller–Plesset (MP2) theory yielded structures exhibiting a cation coordination number of 4, calculations carried out using density functional theory yielded a cation coordination number of 2. Given the above discussion, it becomes apparent that theoretical prediction of the coordination number is to a large extent dependent on the kind of theoretical methodology employed. Therefore, for *ab initio* calculations of complexes containing the larger cations, at least the MP2 or equivalent levels of theory should be employed.

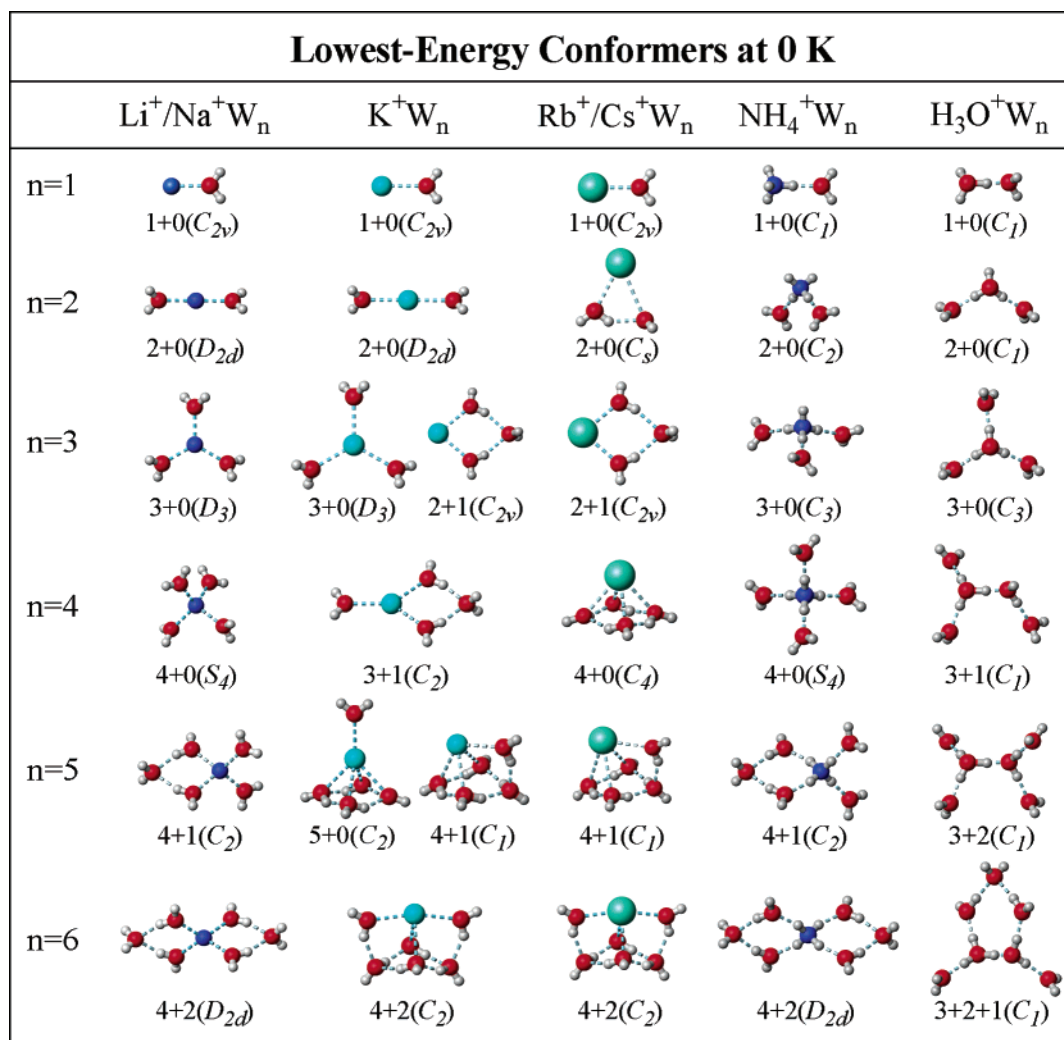
Before we progress any further, it is useful to reiterate that several competing and cooperative interactions contribute to the properties of these solvated cations in the condensed phase.<sup>12,41</sup> In these small cation–water clusters, the structures would result from a competition between hydrogen bonding and ionic interactions.<sup>12,41</sup> The strength of both these interactions, to a large extent, depends on the relative magnitudes of the attractive intermolecular energy components, *viz.*, electrostatic, inductive, dispersive, and the repulsive exchange energies.<sup>42</sup> In a number of recent studies carried out in our group on weakly bound intermolecular complexes, we had highlighted the utility of quantitative estimates of both attractive and repulsive interaction energy components, in obtaining detailed insights into the nature of the intermolecular interaction prevailing in those complexes.<sup>43–50</sup>

Given the absence of such detailed investigations for any of these cation–water complexes, it would be useful to carry out similar calculations on these complexes. Such a study would enable one to obtain quantitative estimates of each of the interaction energy terms, and as a consequence, establish their role in the structural manifestations of these cation–water cluster complexes. Therefore, we initially carried out detailed geometry optimizations on several structures of these cation–water cluster

complexes. Most of the initial structures were obtained from previous theoretical studies.<sup>24–34</sup> In the case of the penta- and hexa-hydrated complexes, we carried out new searches for several other low-lying energy conformers. After ascertaining that the optimized lowest energy structures were genuine minima by evaluating the vibrational frequencies, we carried out a detailed decomposition of the interaction energies using perturbation theory. Given the availability of gas-phase experimental frequencies for the O–H stretch region of some of these complexes, we have also evaluated the anharmonic vibrational frequencies.<sup>51–54</sup> To provide a comprehensive understanding of these intermolecular interactions, the present investigations also included calculations on the water cluster complexes of the ammonium ( $\text{NH}_4^+$ ) and hydronium ( $\text{H}_3\text{O}^+$ ) ions. The calculations on the water clusters of  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  were carried out to highlight the salient similarities/differences in the interactions of metal and organic monocations with varying sizes of water clusters. Apart from providing a detailed insight into the nature of ion-solvation, the present investigations should also be useful in understanding the intricacies of molecular recognition and the *de novo* design of novel molecular systems and functional materials.<sup>12,41,55–58</sup>

## Methods

Given the aims of this study, we employ both supermolecular (SM) variational and perturbational methods in the investigation of these cation–water clusters.<sup>43,59</sup> The former method was employed to carry out the geometry optimizations and evaluate the vibrational frequencies.<sup>60</sup> Most of the SM calculations were carried out at the MP2 level of theory using the augmented correlation consistent (aug-cc-pVDZ) basis set for water and both the hydronium ( $\text{H}_3\text{O}^+$ ), and ammonium ( $\text{NH}_4^+$ ) cations.<sup>61</sup> In the case of metal ions, we employed the correlation consistent (cc-pVDZ) basis set for both  $\text{Li}^+$  and  $\text{Na}^+$ .<sup>61</sup> In case of the  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  ions, we used the energy-adjusted Stuttgart ECPs, and added d exponents to the K (0.48), Rb (0.24), and Cs (0.19) valence bases (henceforth, we refer to them as Stuttgart basis sets).<sup>62</sup> Because one of the referees asked us to elaborate on the role of basis sets in case of the interactions involving larger cations, we also carried out additional calculations using the Feller’s miscellaneous pCVDZ basis set for  $\text{K}^+$ ,<sup>27,63</sup> and the Hay–Wadt and Christiansen’s ECPs for  $\text{Rb}^+$  and  $\text{Cs}^+$ .<sup>64–66</sup> To illustrate the role of basis sets on the magnitudes of each individual energy component, the energy decompositions were carried out using the aug-cc-pVTZ basis set for water and ammonium cation. Though the cc-pVTZ basis set was used for  $\text{Li}^+$  and  $\text{Na}^+$ , Feller’s miscellaneous CVTZ basis sets were used for  $\text{K}^+$ .<sup>27,63,67</sup> To aid the discussion of the results, the basis set of water is used to represent the basis set of the complex. Thus a calculation carried out at the MP2 level using the aug-cc-pVDZ basis set for water and the cc-pVDZ basis for  $\text{Li}^+$  is denoted as MP2/aug-cc-pVDZ. We also carried out density functional theory (DFT) calculations using the B3LYP functional (Becke’s three parameter hybrid functional coupled with the Lee–Yang–Parr correlation functional).<sup>68</sup> In interactions involving the  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  cations, a 50% basis set superposition error (BSSE) correction was made to reproduce more realistic experimental values.<sup>30,43</sup> No BSSE corrections were made for the hydrated alkali-metal ions, because these binding energies tend to be underestimated at the MP2/aug-cc-pVDZ level. Similar observations were made by Feller and co-workers in their study of the water cluster complexes of alkali metal cations.<sup>27</sup> The zero point vibrational energy (ZPE) and thermodynamic corrections were carried out using the frequencies



**Figure 1.** Calculated lowest energy structures of M<sup>+</sup>·(H<sub>2</sub>O)<sub>1-6</sub> (M = Li, Na, K, Rb, Cs, NH<sub>4</sub>, H<sub>3</sub>O) at 0 K.

evaluated at the B3LYP level. Because several earlier studies have indicated that MP2 and B3LYP results are comparable to those obtained using the computationally arduous coupled cluster calculations, we have desisted from carrying out the same.<sup>27</sup>

Even though the SM method is conceptually and computationally simple, it does not offer detailed insight into the forces responsible for the interaction. However, the perturbation method enables one to obtain a physical picture of the interactions prevailing between the various complex monomers.<sup>69-71</sup> This is because in the SM method, the interaction energy is evaluated as the difference of the energy of the complex and the energy of the isolated monomers. However, in perturbational calculations, the interaction energy is obtained as a sum of the individual electrostatic, exchange, dispersion, and induction energies. In the present study, we employed the symmetry adapted perturbation theory (SAPT) method to evaluate the magnitude of each interaction energy component. All the calculations were carried out using the optimized geometries (obtained from SM calculations) of the complexes. The SAPT interaction ( $E_{\text{int}}$ ) is given by

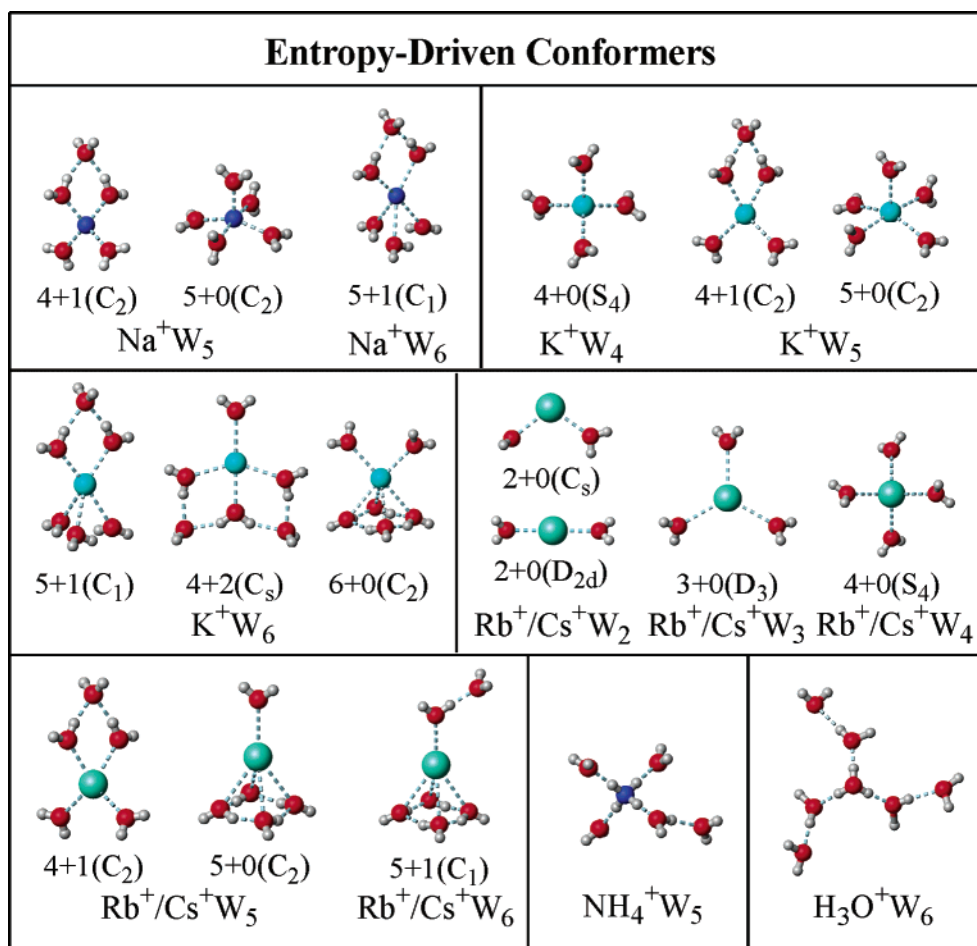
$$E_{\text{int}} = E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)} + \delta_{\text{int}}^{\text{HF}} \quad (1)$$

where  $E_{\text{elst}}^{(1)}$  is the electrostatic energy of the monomers with the unperturbed electron distribution,  $E_{\text{exch}}^{(1)}$  is their first-order

valence repulsion energy due to the Pauli exclusion principle,  $E_{\text{ind}}^{(2)}$  stands for the second-order energy gain resulting from the induction interaction,  $E_{\text{exch-ind}}^{(2)}$  represents the repulsion change due to the electronic cloud deformation,  $E_{\text{disp}}^{(2)}$  is the second-order dispersion energy,  $E_{\text{exch-disp}}^{(2)}$  denotes the second-order correction for a coupling between the exchange-repulsion and the dispersion interaction, and  $\delta_{\text{int}}^{\text{HF}}$  includes the higher order induction and exchange corrections. The exchange terms were evaluated at the coupled cluster singles and doubles level of theory. Because BSSE effects are explicitly included when the SAPT interaction energies are evaluated, a comparison of the BSSE corrected supermolecular interaction energy and the SAPT interaction energy ( $E_{\text{int}}$ ) is appropriate.

To aid the discussion of the results, we have collected all similar interaction energy terms and represent the SAPT interaction energy ( $E_{\text{int}}$ ) as a sum of electrostatic ( $E_{\text{es}}$ ), induction ( $E_{\text{ind}}$ ), dispersion ( $E_{\text{disp}}$ ), and exchange ( $E_{\text{exch}}$ ) terms. Given the size of the systems investigated and the level of theory employed in this study to evaluate the various energy components, it was not feasible to evaluate the computationally demanding higher order components ( $n \leq 3$ ). Hence, one should expect a slight deviation of the total interaction energies evaluated using SAPT and SM calculations. This, however, does not influence the conclusions based on the magnitude of the individual interaction energy components, as was shown in a number of recent papers. A detailed description of SAPT and some of its applications can be found in some recent references.<sup>43-50,69-71</sup>

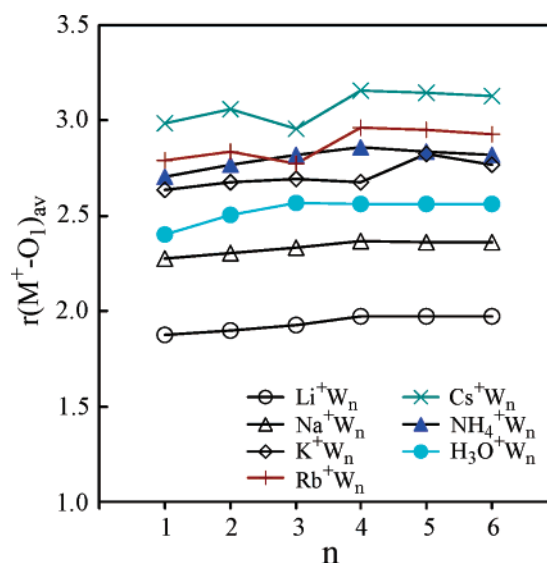




**Figure 2.** Calculated entropy-driven structures of the  $\text{M}^+(\text{H}_2\text{O})_{1-6}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{H}_3\text{O}$ ) complexes at 298 K.

## Results and Discussion

**Structures.** In Figure 1, the optimized structures of the  $\text{M}^+(\text{H}_2\text{O})_{1-6}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{H}_3\text{O}$ ) complexes are displayed. For the sake of brevity, the structures exhibiting the lowest ZPE-corrected internal energy change for the hydration ( $\Delta E_0$ ) and their nearly isoenergetic conformers are only shown. In some cases, the lowest free energy conformers ( $\Delta G_{298}$ ) at 298 K and 1 atm are different from those shown in Figure 1, and therefore we present them in Figure 2. It can readily be seen from Figures 1 and 2, that with few exceptions, the  $\text{Li}^+(\text{H}_2\text{O})_{1-6}$ ,  $\text{Na}^+(\text{H}_2\text{O})_{1-6}$ , and  $\text{NH}_4^+(\text{H}_2\text{O})_{1-6}$  cluster complexes exhibit a strong structural semblance. On a similar note, there are no differences in the gross structural features of the water cluster complexes of  $\text{Rb}^+$  and  $\text{Cs}^+$ . It can also be seen from Figure 1 that the trihydrated complexes of  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  herald the onset of the secondary solvent shell. The tetrahydrated complexes of  $\text{Rb}^+$  and  $\text{Cs}^+$  merit mention, because the lowest energy structures are very similar to those of the corresponding water tetramer. However, the presence of the cation leads to a small increase in the intermolecular O—O distances ( $\text{Rb}^+(\text{H}_2\text{O})_4$ , 0.007 Å;  $\text{Cs}^+(\text{H}_2\text{O})_4$ , 0.003 Å). Unlike the water cluster complexes of  $\text{Ag}^+$  or  $\pi$ -systems,<sup>40,44</sup> there are perceptibly small differences in the structures obtained after geometry optimization at the B3LYP and MP2 levels. However, these differences are significantly larger for complexes involving the larger cations,  $\text{Rb}^+$  and  $\text{Cs}^+$ , the details of which will be presented elsewhere.<sup>72</sup> A detailed description of various conformers of some of these cation—water complexes can, however, be found in some of our earlier work and the work of Feller and co-workers.<sup>25–30</sup>



**Figure 3.** Trends in the calculated  $R_{\text{M}^+-\text{O}}$  distance (Å) for all the  $\text{M}^+(\text{H}_2\text{O})_{1-6}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{H}_3\text{O}$ ) complexes (MP2/aug-cc-pVDZ level for water,  $\text{NH}_4^+$ , and  $\text{H}_3\text{O}^+$ ; cc-pVDZ for  $\text{Li}^+$  and  $\text{Na}^+$ ; Stuttgart basis sets for  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ ).

Expectedly, the complexation with the cation leads to an increase in the OH bond lengths of the water molecule. One also notes from Figure 3 that the average cation—water distances ( $R_{\text{M}^+-\text{O}}$ ) are nearly constant for all the cation—water complexes investigated in this study. It can also be seen that the onset of the secondary solvent shell in the trihydrated complexes of  $\text{Cs}^+$  and  $\text{Rb}^+$  is marked by a sharp decrease in the average cation—

**TABLE 1: Comparison of Calculated and Experimental Enthalpies of Various Cation-Water Clusters<sup>a</sup>**

<i>n</i>	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	H <sub>3</sub> O <sup>+</sup>
$-\Delta E_0$							
1	30.7 [1+0( <i>C<sub>2v</sub></i> )]	23.0 [1+0( <i>C<sub>2v</sub></i> )]	17.0 [1+0( <i>C<sub>2v</sub></i> )]	14.6 [1+0( <i>C<sub>2v</sub></i> )]	13.2 [1+0( <i>C<sub>2v</sub></i> )]	18.3 [1+0( <i>C<sub>i</sub></i> )]	32.2 [1+0]
2	58.0 [2+0( <i>D<sub>2d</sub></i> )]	43.3 [2+0( <i>D<sub>2d</sub></i> )]	32.2 [2+0( <i>D<sub>2d</sub></i> )]	27.7 [2+0( <i>C<sub>s</sub></i> )]	24.5 [2+0( <i>C<sub>i</sub></i> )]	33.3 [2+0( <i>C<sub>2</sub></i> )]	52.7 [2+0]
3	78.8 [3+0( <i>D<sub>3</sub></i> )]	60.4 [3+0( <i>D<sub>3</sub></i> )]	45.6 [3+0( <i>D<sub>3</sub></i> )]	39.7 [2+1( <i>C<sub>2v</sub></i> )]	36.9 [2+1( <i>C<sub>2v</sub></i> )]	46.1 [3+0( <i>C<sub>3</sub></i> )]	69.6 [3+0]
4	94.7 [4+0( <i>S<sub>d</sub></i> )]	74.4 [4+0( <i>S<sub>d</sub></i> )]	57.7 [3+1( <i>C<sub>2</sub></i> )]	51.5 [4+0( <i>C<sub>d</sub></i> )]	49.4 [4+0( <i>C<sub>d</sub></i> )]	57.0 [4+0( <i>S<sub>d</sub></i> )]	80.8 [3+1]
5	107.1 [4+1( <i>C<sub>2</sub></i> )]	85.6 [4+1( <i>C<sub>2</sub></i> )]	69.4 [5+0( <i>C<sub>2</sub></i> )]	62.9 [4+1( <i>C<sub>i</sub></i> )]	60.2 [4+1( <i>C<sub>i</sub></i> )]	66.9 [4+1( <i>C<sub>2</sub></i> )]	92.1 [3+2]
6	118.7 [4+2( <i>D<sub>2d</sub></i> )]	96.4 [4+2( <i>D<sub>2d</sub></i> )]	81.4 [4+2( <i>C<sub>2</sub></i> )]	73.9 [4+2( <i>C<sub>2</sub></i> )]	70.3 [4+2( <i>C<sub>2</sub></i> )]	76.1 [4+2( <i>D<sub>2d</sub></i> )]	101.6 [3+2+1]
$-\Delta G_{298}$							
1	24.9 [25.5]	17.3 [17.6]	11.6 [11.4]	9.3 [9.6]	8.0 [7.9]	12.7 [13.0,11.3]	25.3 [24.3,24.6,22.9]
2	44.9 [44.4]	31.5 [30.8]	20.6 [20.3]	17.0 [16.6]	14.5 [13.8]	20.2 [19.1,19.5]	39.4 [37.3,37.4,37.9]
3	58.0 [57.7]	41.4 [40.1]	28.3 [26.6]	22.6 [21.6]	18.8 [18.0]	26.8 [24.4,25.4]	47.7 [46.8,46.9,46.4]
4	66.6 [65.2]	48.9 [46.4]	32.9 [31.0]	26.2 [25.4]	22.6 [21.0]	29.9 [27.2,29.5]	52.1 [52.5,52.5,50.9]
5	69.2 [69.7]	51.1 [50.3]	35.9 [34.2]	27.3 [28.2]	23.8 [- - -]	30.1 [31.5,32.5]	57.0 [56.6,57.0,54.4]
6	71.9 [72.2]	53.6 [53.2]	36.8 [36.5]	27.9 [- - -]	24.7 [- - -]	32.7 [33.8, - - -]	58.0 [- - -,59.6, - - -]
$-\Delta H_{298}$							
1	31.7 [34.0]	23.8 [24.0,22.6]	17.7 [17.9]	15.2 [15.9]	13.8 [13.7]	19.5 [19.9,17.3]	33.4 [31.8,31.6,33.0]
2	59.3 [59.8]	44.2 [43.8,42.2]	32.7 [34.0]	28.7 [29.5]	25.6 [26.2]	34.7 [32.3,32.0]	54.2 [50.8,51.1,54.0]
3	80.5 [80.5]	61.5 [59.6,59.0]	46.1 [47.2]	41.5 [41.7]	37.6 [37.4]	47.0 [44.5,45.4]	71.4 [68.4,68.6,70.8]
4	96.5 [96.9]	75.5 [73.4,72.1]	57.6 [59.0]	54.3 [52.9]	52.3 [48.0]	57.8 [55.3,57.6]	83.1 [79.9,81.3,83.7]
5	110.0 [110.8]	86.5 [85.7, - - -]	68.6 [69.7]	66.4 [63.4]	63.7 [- - -]	69.3 [65.9,67.3]	94.3 [91.0,92.9,92.2]
6	121.0 [122.9]	95.0 [96.4, - - -]	81.7 [79.7]	77.9 [- - -]	74.2 [- - -]	79.1 [75.0, - - -]	104.9 [- - -,103.6, - - -]

<sup>a</sup> All energies are in units of kcal/mol. All calculations were carried out at the MP2 level. The water basis set used aug-cc-pVDZ except for the Na<sup>+</sup> and K<sup>+</sup> containing clusters, which were carried out using TZ3P and TZ2P basis sets, respectively, in our previous works (refs 30 and 31) wherein the binding energies were calculated at the MP2 level with HF/TZ2P thermal energies. For the basis set of the alkali metal ions, the Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> used cc-pVDZ, [6s5p2d], and [8s7p3d], respectively, and both Rb<sup>+</sup> and Cs<sup>+</sup> used the Stuttgart basis set. Although a 50% BSSE correction was applied to obtain the energies for the hydrogen-bonded clusters (hydrated NH<sub>4</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup>), no BSSE corrections were applied for the alkali metal cation containing complexes. The experimental enthalpies for the Li<sup>+</sup> complexes are from ref 2b, for Na<sup>+</sup> from refs 2b and 2e, for K<sup>+</sup> from ref 2b, for Cs<sup>+</sup> from ref 2b, for NH<sub>4</sub><sup>+</sup> from ref 5, and for H<sub>3</sub>O<sup>+</sup> from refs 4 and 6.

water distances. It is interesting to note that  $R_{\text{NH}_4^+-\text{O}}$  is similar to  $R_{\text{K}^+-\text{O}}$ , whereas  $R_{\text{H}_3\text{O}^+-\text{O}}$  is between  $R_{\text{Na}^+-\text{O}}$  and  $R_{\text{K}^+-\text{O}}$ .

**Energies.** With this background on the structures, it is useful to examine the energies of these cation-water cluster complexes. In Table 1, we present a comparison of calculated and experimental enthalpies ( $\Delta H_{298}$ ) of some of the complexes investigated in this study.<sup>3-6</sup> The ZPE corrected binding energies ( $-\Delta E_0$ ) and free energies ( $\Delta G_{298}$ ) are also given to emphasize the role of thermal corrections. Before we proceed further, we would like to briefly elaborate on the strategy we have employed to obtain the calculated enthalpies. In principle, a comparison of the calculated and experimental quantities (enthalpies and vibrational frequencies) is appropriate using the energies obtained at similar levels of theory and the same basis sets. However, the absence of similar basis sets and the widely differing characteristics of the alkali metal and organic cations implies that one has to use different basis sets to carry out the calculations. Additionally, one also has to confront the problem of BSSE, while evaluating the interaction energies. Fortunately, interactions involving metallic cations exhibit very small BSSE effects. As a result, the BSSE uncorrected interaction energies were generally employed for comparison with the experiment.<sup>26,27,30,31</sup> However, things are dramatically different in interactions involving the organic cations such as H<sub>3</sub>O<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, wherein the interaction of the cation with the water molecule is mediated through the hydrogen atom. In the context of one of the referee's comments on our use of different BSSE corrections, we would like to mention that intermolecular interactions mediated through hydrogen atoms generally require very large basis sets to minimize the errors in the interaction energies arising from both BSSE (basis set superposition error) and BSIE (basis set incompleteness error) effects. The large size of the larger H<sub>3</sub>O<sup>+</sup> and NH<sub>4</sub><sup>+</sup> clusters, however, precludes calculations using large basis sets. Thus, for a comparison of the calculated numbers to experimental quantities, we have often found it useful to employ moderately sized basis sets and a 50%

**TABLE 2: Calculated (MP2/aug-cc-pVDZ) Interaction Energies ( $-\Delta E_0$ ), of All the M<sup>+</sup>·(H<sub>2</sub>O)<sub>*n*</sub> Complexes<sup>a</sup>**

<i>n</i>	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	H <sub>3</sub> O <sup>+</sup>
1	30.7	20.7	13.7 (15.6)	12.4 (14.6)	10.9 (13.2)	18.3	32.2
2	58.0	39.5	26.3 (29.6)	22.4 (27.7)	19.5 (24.5)	33.3	52.9
3	78.8	54.9	37.7 (42.0)	35.1 (39.7)	32.1 (36.9)	46.1	69.6
4	94.7	67.9	48.6 (53.9)	45.8 (51.3)	44.1 (49.4)	57.0	80.8
5	107.1	79.7	58.8 (64.3)	56.8 (62.9)	54.0 (60.2)	66.9	92.1
6	118.7	91.1	70.2 (76.7)	67.5 (73.9)	63.6 (70.3)	76.1	101.6

<sup>a</sup> All energies are in kcal/mol. In the case of alkali metal ions, the basis sets used are cc-pVDZ for both Li<sup>+</sup> and Na<sup>+</sup>, pCVDZ for K<sup>+</sup>, and the Hay-Wadt and Christiansen ECPs for Rb<sup>+</sup> and Cs<sup>+</sup>. The ZPE corrections were made using the B3LYP/aug-cc-pVDZ frequencies. The values in parentheses were obtained using Stuttgart basis sets for K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>. Although a 50% BSSE correction was made for both the NH<sub>4</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup> H-bonded complexes, the energies of the alkali metal cation complexes were not corrected for BSSE.

BSSE correction. A detailed justification for the use of a 50% BSSE correction is given in ref 43. It should be noted that even in the case of the interaction energy of the water dimer, a number of authors<sup>73</sup> have employed the median of the BSSE corrected and uncorrected interaction energies, for comparison with experiment. Therefore, when they were compared with experiment, the calculated interaction energies involving metallic cation water clusters were not corrected for BSSE effects. However, in interactions involving the organic cations, we have used the 50% BSSE corrected interaction energies for comparison with experiment.

Apart from highlighting the good agreement of the experimental and calculated enthalpies, the data presented in Table 1 indicate that thermal corrections are relatively smaller for clusters containing the larger cations. However, it should be noted that the calculated thermodynamic properties depend highly on the basis set employed, and the reported values in Table 1 were obtained using large basis sets for Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. We elaborate on this role of basis sets subsequently.

**TABLE 3: Interaction Energy Components of All the  $M^+(H_2O)_1$  Complexes Obtained Using the aug-cc-pVDZ and aug-cc-pVTZ Basis Sets<sup>a</sup>**

$E_{\text{com}}$	aug-cc-pVDZ						aug-cc-pVTZ			
	$Li^+$	$Na^+$	$K^+$	$Rb^+$	$Cs^+$	$NH_4^+$	$Li^+$	$Na^+$	$K^+$	$NH_4^+$
$E_{\text{int}}^b$	-33.15	-22.77	-16.29 (-16.78)	-13.63 (-14.94)	-11.81 (-13.14)	-19.87	-34.42	-23.29	-17.64	-21.04
$E_{\text{es}}$	-31.72	-23.84	-16.81 (-18.39)	-15.06 (-16.81)	-12.96 (-15.28)	-23.81	-32.37	-23.81	-18.79	-24.21
$E_{\text{exch}}$	10.67	7.83	4.80 (7.18)	5.16 (7.17)	4.18 (7.48)	15.60	10.92	7.70	7.10	15.32
$E_{\text{ind}}$	-11.89	-6.59	-3.48 (-4.17)	-2.85 (-3.75)	-2.11 (-3.63)	-8.12	12.42	-6.81	-4.28	-8.16
$E_{\text{disp}}$	-0.22	-0.16	-0.80 (-1.39)	-0.87 (-1.55)	-0.91 (-1.71)	-3.54	-0.54	0.36	-1.67	-3.99

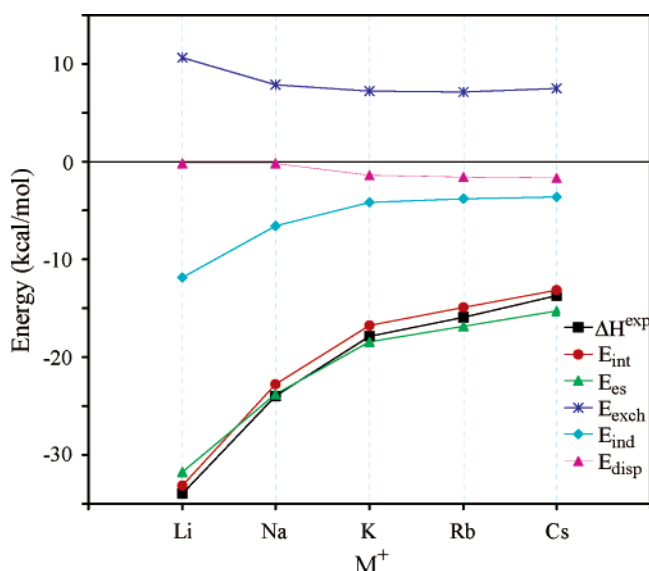
<sup>a</sup> All energies are in kcal/mol. In the case of alkali metal ions, the basis sets used are cc-pVDZ for both  $Li^+$  and  $Na^+$ , pCVDZ for  $K^+$ , and the Hay–Wadt and Christiansen ECPs for  $Rb^+$  and  $Cs^+$ . The values in parentheses were obtained using the Stuttgart basis sets for  $K^+$ ,  $Rb^+$ , and  $Cs^+$ .

<sup>b</sup>  $E_{\text{int}} = E_{\text{es}} + E_{\text{exch}} + E_{\text{ind}} + E_{\text{disp}}$ .

**TABLE 4: MP2 Equivalent Interaction Energy Components of Different Conformers of the  $(M^+ \cdot H_2O) - H_2O$  Complexes Obtained Using the aug-cc-pVDZ Basis Set<sup>a</sup>**

	$Li^+ (D_{2d})$	$Na^+ (D_{2d})$	$K^+ (D_{2d})$	$Rb^+ (C_s)$	$Cs^+ (C_s)$
$E_{\text{int}}$	-29.02	-20.68	-14.89 (-15.03)	-13.55 (-14.26)	-10.99 (-13.51)
$E_{\text{es}}$	-28.36	-21.82	-15.42 (-16.60)	-15.31 (-16.06)	-14.96 (-15.74)
$E_{\text{exch}}$	9.67	6.99	4.33 (6.36)	6.23 (7.03)	10.05 (7.85)
$E_{\text{ind}}$	-9.81	-5.61	-3.00 (-3.45)	-2.53 (-2.89)	-3.34 (-2.95)
$E_{\text{disp}}$	-0.52	-0.24	-0.81 (-1.33)	-1.94 (-2.34)	-2.74 (-2.67)

<sup>a</sup> See the footnote of Table 3 for units and definitions.



**Figure 4.** Calculated interaction energy components of the  $M^+(H_2O)_1$  ( $M = Li, Na, K, Rb, Cs$ ) complexes (same basis sets in those of Figure 3).

Though the data presented in Table 1 illustrate a good agreement of the calculated and experimental thermodynamic properties, we carried out calculations at the MP2/aug-cc-pVDZ level of theory to allow a consistent comparison of the calculated energies. The ZPE corrected binding energies ( $-\Delta E_0$ ) obtained at the MP2/aug-cc-pVDZ level are therefore presented in Table 2. It should be noted that, in most cases, the lowest energy conformers (Tables 1 and 2) are similar, even though the relative energies are significantly different. This indicates that the use of different basis sets has a small effect on the relative stabilities of the various conformers. In particular, Tables 1 and 2 indicate that the interaction energies decrease as the size of the metal cation increases. The binding energies of water cluster complexes of  $NH_4^+$  are higher than those of  $K^+$ , despite the fact that both of them possess very similar ionic radii. We have discussed this issue in more detail in the context of our work on cation- $\pi$  interactions.<sup>44</sup> The incremental enthalpies of these cation–water complexes approach a constant value ( $\sim 10$  kcal/mol), which is close to the bulk ice/water binding energy.<sup>74</sup>

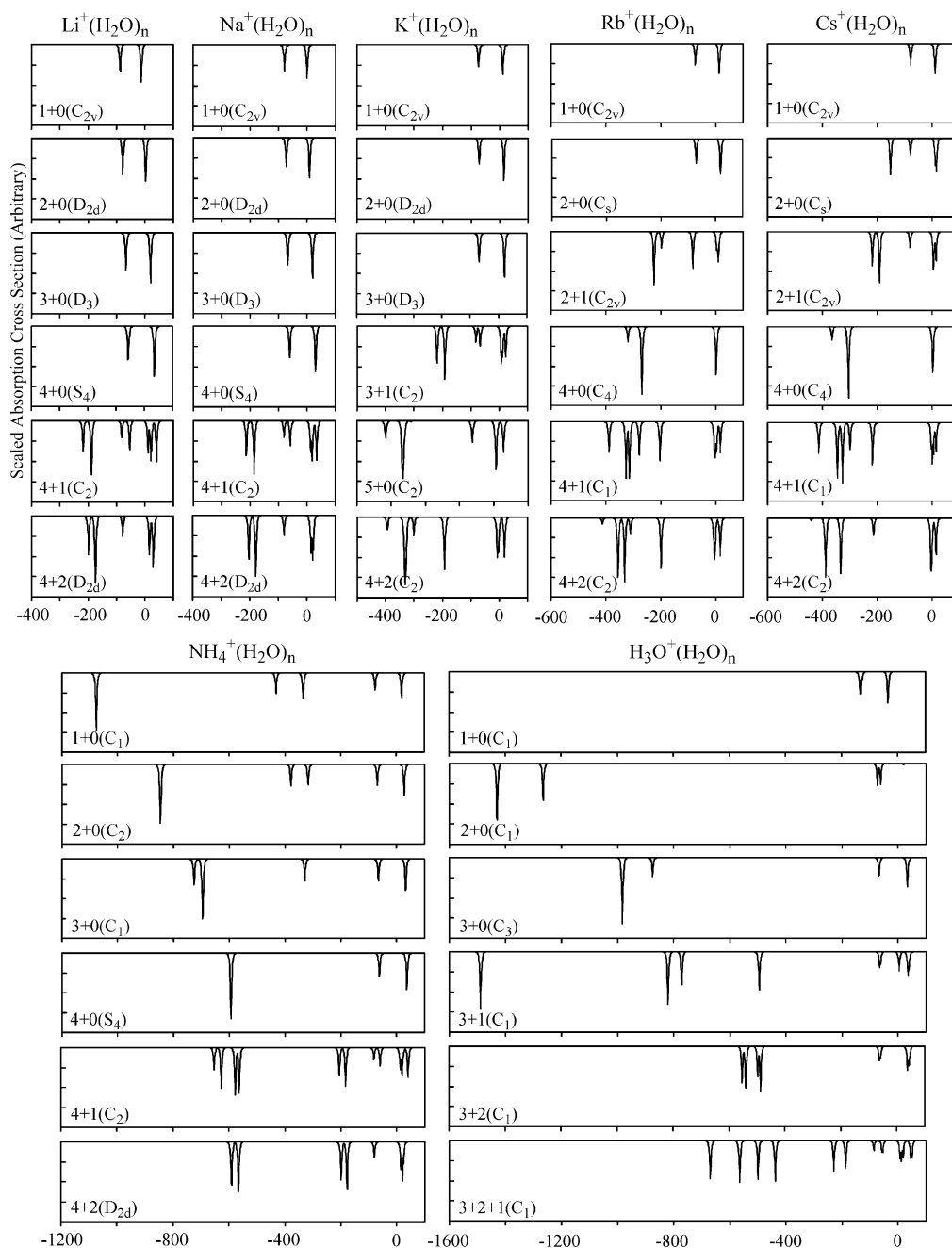
**TABLE 5: MP2 Equivalent Interaction Energy Components of  $C_s$  and  $D_{2d}$  Conformers of the  $(K^+ \cdot H_2O) - H_2O$ ,  $(Rb^+ \cdot H_2O) - H_2O$ , and  $(Cs^+ \cdot H_2O) - H_2O$  Complexes<sup>a</sup>**

	$(K^+ \cdot H_2O) - H_2O$		$(Rb^+ \cdot H_2O) - H_2O$		$(Cs^+ \cdot H_2O) - H_2O$	
	$D_{2d}$	$C_s$	$D_{2d}$	$C_s$	$D_{2d}$	$C_s$
$E_{\text{es}}$	-16.60	-13.87	-16.06	-13.47	-15.74	-13.51
$E_{\text{exch}}$	6.36	4.44	7.03	6.55	7.85	7.85
$E_{\text{ind}}$	-3.45	-2.66	-2.89	-2.89	-2.95	-2.95
$E_{\text{disp}}$	-1.33	-1.23	-2.34	-1.62	-2.67	-2.67
$E_{\text{int}}$	-15.03	-13.31	-14.26	-11.43	-13.51	-13.51

<sup>a</sup> See the footnote of Table 3 for units and definitions. The energies were obtained using the Stuttgart basis sets for  $K^+$ ,  $Rb^+$ , and  $Cs^+$ , and the aug-cc-pVDZ basis set for water.

At this juncture, it is interesting to mention the case of the dihydrated complexes of  $Rb^+$  and  $Cs^+$ . Earlier and more recently, our calculations seem to indicate that the  $C_s$  conformer, which exhibits the presence of a nascent intermolecular water–water hydrogen bond, is more stable than the  $D_{2d}$  conformer.<sup>27,72</sup> This reversal of conformer stability as we progress from  $K^+(H_2O)_2$  to  $Rb^+(H_2O)_2$  is particularly intriguing. We dwell on the origin of this stability subsequently.

Because, to our knowledge, there have been no studies on the magnitudes of the interaction energy components of any of these cation–water complexes, we begin our discussion with the binding of these cations to a single water molecule (Table 3, Figure 4). The broad consensus on the predominance of electrostatic energies in the binding of these cations to water molecules is well illustrated in Figure 4. In particular, it can be seen that the magnitude of electrostatic energies ( $E_{\text{es}}$ ) mirrors both the total interaction energies ( $E_{\text{int}}$ ) and the experimental enthalpies ( $\Delta H^{\text{exp}}$ ). For smaller cations, two things happen as a result of the shorter intermolecular distances: (i) the repulsive exchange ( $E_{\text{exch}}$ ) energies increase, and (ii) the attractive induction ( $E_{\text{ind}}$ ) energies increase. It should be noted that the induction energies can be attributed to the charge redistribution of the water molecule (i.e., charge transfer from the oxygen to the hydrogen atoms) so that the interaction energy is maximized with the enhanced dipole moment of the water molecule. As will be seen later, the magnitude of these induction energies can also be correlated to the infrared intensities of the OH stretching modes. Hitherto, our discussion has largely neglected



**Figure 5.** Calculated vibrational frequency shifts ( $\text{cm}^{-1}$ ) of the  $-\text{OH}$  stretching mode in all the  $\text{M}^+(\text{H}_2\text{O})_{1-6}$  complexes (the lowest energy structures at 0 K). The shifts are with respect to the average of the frequencies of the symmetric and asymmetric  $-\text{OH}$  stretching modes of an isolated water monomer (same basis sets in those of Figure 3).

the contribution of dispersion energies, which is negligible, as can be seen in the case of interactions involving the smaller cations. However, the contribution of dispersion energies to the total attractive energy gradually increases as we progress from  $\text{Li}^+$  to  $\text{Cs}^+$ . In light of one of the referee's comments, we have obtained the magnitudes of the interaction energy components using both the larger aug-cc-pVTZ basis set for water and different ECPs in the case of the cations. It can be seen from Table 3, that the magnitude of the total interaction energy ( $E_{\text{int}}$ ) of the  $\text{Li}^+-\text{H}_2\text{O}$  and  $\text{Na}^+-\text{H}_2\text{O}$  complexes is nearly independent of the nature of the basis set; i.e., the use of a larger basis set does not lead to substantial changes either in the magnitude of the total interaction energy or the individual interaction energy components. Things are, however, dramatically different in interactions involving the water cluster complexes of the larger alkali metal cations. Thus, in the  $\text{K}^+-\text{H}_2\text{O}$  complex, the use of

the aug-cc-pVTZ basis set leads to an increase in the magnitude of nearly all the interaction energy components ( $E_{\text{es}}$  increases by  $\sim 12\%$ ;  $E_{\text{ind}}$  increases by  $\sim 23\%$ ,  $E_{\text{exch}}$  increases by  $\sim 48\%$ , and  $E_{\text{disp}}$  increases by  $\sim 108\%$ ), as well as the total interaction energy ( $E_{\text{int}}$  increases by  $\sim 8\%$ ). The role of electron correlation in describing the interactions of the larger cations can readily be noted from the percentage increase in the magnitude of dispersion energies. A more interesting observation is that similar increases in each of these interaction energy components can be obtained by using a different basis set for the  $\text{K}^+$  cation and the aug-cc-pVDZ basis set for water.

Against this background, it is instructive to examine the interactions of the ammonium cation with the water molecule. Though the  $\text{NH}_4^+$  and  $\text{K}^+$  cations have nearly similar ionic radii, the polarizability of the former ( $\alpha = 8.83$  au) is larger than that of the latter ( $\alpha = 5.52$  au).<sup>75,76</sup> Given the relationship



**TABLE 6: Calculated MP2/aug-cc-pVDZ Anharmonic and Harmonic Frequencies of the OH Stretching and Intermolecular ( $S_z$ ) Modes of the  $M^+\cdot H_2O$  Complexes<sup>a</sup>**

	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	H <sub>2</sub> O
Anharmonic							
$\nu_3$	3669	3687	3699 (3693)	3700 (3693)	3701 (3689)	3693	3744
$\nu_1$	3585	3598	3604 (3598)	3700 (3596)	3602 (3590)	3593	3621
$\nu_2$	1626	1622	1618 (1618)	1616 (1617)	1613 (1615)	1589	1573
$S_z$	506	277	182 (201)	146 (176)	129 (154)	287	
Harmonic							
$\nu_3$	3871 <sub>21</sub>	3887 <sub>16</sub>	3899 <sub>13</sub> (3892 <sub>14</sub> )	3899 <sub>13</sub> (3891 <sub>13</sub> )	3899 <sub>12</sub> (3887 <sub>12</sub> )	3894 <sub>17</sub>	3938 <sub>7</sub>
$\nu_1$	3773 <sub>9</sub>	3785 <sub>5</sub>	3789 <sub>4</sub> (3784 <sub>4</sub> )	3789 <sub>4</sub> (3781 <sub>4</sub> )	3787 <sub>3</sub> (3775 <sub>4</sub> )	3778 <sub>6</sub>	3804 <sub>0</sub>
$\nu_2$	1661 <sub>10</sub>	1659 <sub>9</sub>	1658 <sub>9</sub> (1658 <sub>9</sub> )	1656 <sub>8</sub> (1658 <sub>8</sub> )	1652 <sub>8</sub> (1657 <sub>8</sub> )	1640 <sub>4</sub>	1622 <sub>7</sub>
$S_z$	530 <sub>11</sub>	290 <sub>3</sub>	191 <sub>1</sub> (210 <sub>1</sub> )	153 <sub>0</sub> (184 <sub>1</sub> )	135 <sub>0</sub> (161 <sub>1</sub> )	302 <sub>8</sub>	

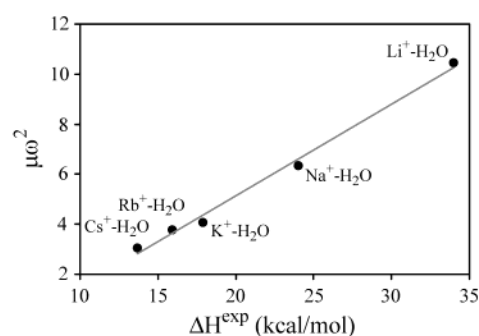
<sup>a</sup> All frequencies are in cm<sup>-1</sup>. The harmonic IR intensities (10 km/mol) are given as subscripts. See the footnote of Table 2 for the basis sets.

<sup>b</sup> The experimental  $\nu_3$  and  $\nu_1$  for the Cs<sup>+</sup>·H<sub>2</sub>O complex are 3758 (20), and 3636 (3) cm<sup>-1</sup>, respectively.<sup>19</sup>

between polarizabilities and dispersion energies,<sup>42</sup> this indicates that the magnitude of dispersion energies would be quite substantial in the case of interactions involving the NH<sub>4</sub><sup>+</sup> cation. Given our recent investigations of these cations in the context of cation- $\pi$  interactions,<sup>44</sup> one may expect that the electrostatic and induction energies of NH<sub>4</sub><sup>+</sup>·H<sub>2</sub>O would be similar to those of K<sup>+</sup>·H<sub>2</sub>O complex. However, the magnitude of the electrostatic and induction energies in the case of the NH<sub>4</sub><sup>+</sup>·H<sub>2</sub>O complex is nearly 1.4 and 2.3 times (or 7.0 and 3.6 kcal/mol) higher than the values observed in the K<sup>+</sup>·H<sub>2</sub>O complex, respectively (Table 3). The H atom in NH<sub>4</sub><sup>+</sup>, which is interacting with the O atom in the water molecule by H-bonding is responsible for these enhanced energies.

It is instructive to examine the nature of binding of the second water molecule to the cation-water monomer complex (Table 4). It becomes evident from these calculations of the (M<sup>+</sup>-H<sub>2</sub>O)·H<sub>2</sub>O interaction energies that the binding of the second water molecule to the (M<sup>+</sup>-H<sub>2</sub>O) complex is nearly as strong as the binding of a single water molecule to a bare cation. Important differences, however, emerge in the magnitude of the individual interaction energy components. Although there is a decrease in magnitude of the electrostatic, induction, and repulsive exchange energies, there is a small increase in the magnitude of the dispersion energies. This increase is more pronounced in the more stable  $C_s$  conformer of the Rb<sup>+</sup> (H<sub>2</sub>O)<sub>2</sub> and Cs<sup>+</sup> (H<sub>2</sub>O)<sub>2</sub> complexes due to the water-water interaction. To explain the stability of the  $C_s$  conformers of the Rb<sup>+</sup>·(H<sub>2</sub>O)<sub>2</sub> and Cs<sup>+</sup>·(H<sub>2</sub>O)<sub>2</sub> complexes over that of the corresponding  $D_{2d}$  conformers, we present a comparison of the interaction energy components of the  $C_s$  and  $D_{2d}$  conformers of the K<sup>+</sup>·(H<sub>2</sub>O)<sub>2</sub>, Rb<sup>+</sup>·(H<sub>2</sub>O)<sub>2</sub>, and Cs<sup>+</sup>·(H<sub>2</sub>O)<sub>2</sub> complexes in Table 5. We believe that this conformational preference is due to the enhanced electrostatic and dispersion energies observed in case of the  $C_s$  conformers of the water dimer complexes of the larger cations. For K<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub>, the  $C_s$  conformer merges into the  $D_{2d}$  conformer. A more detailed explanation of this conformational preference will be presented elsewhere.<sup>72</sup>

**Vibrational Frequencies.** Most of the experimental data on vibrational frequencies is based on the observations of the -OH stretching modes of these ion-water clusters.<sup>1,19,20</sup> Though it is desirable to carry out a detailed analysis of the vibrational spectra of these ion-water clusters, such a task requires a detailed comparison of the spectra of several conformers for different cluster sizes. However, in the context of this paper wherein we discuss the trends in the properties of lowest energy structures of these ion-waters, it is useful to examine the -OH vibrational spectra as a function of both cluster size and the nature of the cation. Figure 5 wherein we have plotted the shifts in the calculated -OH harmonic vibrational spectra (with respect



**Figure 6.** Calculated force constant ( $k = \mu\omega^2$  in (dyne cm<sup>-1</sup>);  $\mu$ , reduced mass;  $\omega$ , frequency) for the intermolecular stretching mode ( $S_z$ ) vs experimental enthalpy (same basis sets in those of Figure 3).

to the average of the asymmetric and symmetric stretches of the water monomer) indicates that the magnitude of -OH red shifts increases with both an increase in cluster size and an increase in the size of the metal cation. This is very much unlike the interactions of solvated anions, wherein the more strongly bound anions induce much larger red shifts. The significantly larger red shifts observed in clusters containing the larger cations can also be attributed to the formation of water-water hydrogen bonds. One can readily note that the vibrational spectra give a lot of insight into the structure of the ion-water cluster. In particular, they provide valuable clues to the emergence of an intermolecular water-water hydrogen bond. Thus, though an intermolecular water-water hydrogen bond appears in clusters ( $n > 4$ ) for Li<sup>+</sup> and Na<sup>+</sup>, it emerges much sooner for both Rb<sup>+</sup> and Cs<sup>+</sup>. Unlike ion-water clusters involving metal cations, the clusters involving organic cations exhibit much larger red shifts. Additionally, the magnitude of red shift decreases with an increase in the cluster size.

Because there have been no reports of the anharmonic frequencies for the cation-water monomer complexes, we have presented them in Table 6. It is interesting to note that the magnitude of the intermolecular stretching mode ( $S_z$ ) [ $\mu\omega^2$ : force constant or the frequency square multiplied by the reduced mass of the cation and the water molecule] is correlated to the strength of the ion-water interaction. The linear relation of the calculated anharmonic  $S_z$  mode and the experimental enthalpies (Figure 6) indicates that one could obtain reasonably accurate estimates of the experimental enthalpies based on knowledge of the anharmonic  $S_z$  mode.

## Concluding Remarks

The present theoretical study yields several insights into the nature of interactions prevalent in small cation-(water)<sub>*n*</sub> ( $n =$

1-6) clusters. Apart from providing the most consistent theoretical comparison of cation-water interactions involving various kinds of monovalent cations, we have also provided a detailed description of the magnitudes of the interaction energy components of the cation-water interactions. This, we believe, would enable one to obtain a thorough understanding of ion-specific recognition and its utility in designing novel molecular systems and functional materials.<sup>77</sup> It would also promote the development of new potential models to describe ion-water interactions. In particular, the energy components of the interaction energies will be valuable in understanding the myriad structural manifestations of these small ion-water clusters and host-guest complexes. Given the current interest in biological and chemical systems, the present study would also help obtain a better perspective of noncovalent intermolecular interactions.

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